PHYSICO-CHEMICAL METHODS

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AUTHORIZED TRANSLATION

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With Ninety-seven Illustrations

PHILADELPHIA

P. BLAKISTON'S SON & CO.

1012 WALNUT STREET

1898

PREFACE.

In the preface to the German edition the author calls attention to the ever-widening application of physico-chemical methods in the various branches of chemistry. He says the vapor density, melting point, boiling point, and specific gravity are no longer the only constants the determination of which is necessary in organic chemistry. The electric conductivity, specific refraction, thermal constants, depression of the freezing point and vapor pressure, etc., are of fundamental importance in determining the constitution and molecular weight of substances, as well as in determining their identity and degree of purity.

The theoretical significance of physico-chemical constants, and the fact that their application has been extended to almost every branch of chemistry, renders it desirable, if not necessary, for all students of the science to become more or less familiar with the methods of measurement.

In this book the author has systematized the more important physico-chemical methods. The very complete descriptions of apparatus and the minute details in the methods of operation, as well as the large number of references given throughout the book, seem to warrant its translation.

In the preparation of the English edition no additions have been made to the text. The few references which have been added are inclosed in brackets.

THE TRANSLATOR.

CONTENTS.

I. THE CHEMICAL BALANCE.

General Rules for Weighing.—The balance is placed so that it is protected from the direct rays of the sun and other sources of heat which would produce an inequality of temperature in the different parts.

It must also be free from the influence of vibrations.

The balance is brought into a horizontal position by means of foot-screws on the bottom of the case. The horizontality is indicated by a spirit-level or a plumb-line.

The interior of the balance case is always kept dry by means of calcium chloride, etc.

With constant load a good balance should always take the same position when allowed to come to rest. The extent of the swing for any load should diminish slowly.

After the arrestment of the balance the pointer should remain at the middle division of the scale; in raising the arrestment the two supports of the beam should be removed at the same instant. In regard to the equality in the length of the two arms, see page 11.

The weights should be placed on the balance only after the arrestment of the beam, and should in no case be touched with the fingers. Rapid swinging of the beam will cause error in the weighing. For accurate weighing, the balance case should be kept closed.

Adjustment of the Balance.—The sensibility and hence the vibration period of the balance are regulated by means of a gravity-bob situated near the middle of the pointer. The adjustment is so made that the vibration period for a short-armed balance is from six to ten seconds, and from ten to fifteen seconds for a long-armed balance.

The adjustment of the balance so that the pointer will swing equal distances on both sides of the middle division of the scale is made by means of movable weights attached to the ends of the

beam or, when these fail, the unsymmetrical weight at the middle of the beam is given such a position that the inequality in the weights of the two arms is counterbalanced.

Determination of the Resting Point. Method of Weighing.—It is not necessary nor desirable in weighing, that the weights be adjusted so that the pointer will swing equal distances on both sides of the middle division of the scale; *e. g.*, if 10 is the middle division, the resting point may be 9 or 9.5.

The resting point is calculated from several turning points of the pointer. The arithmetic mean of the turning points is taken for each side, and the mean of these two is taken as the resting point. The first and last observation used in the calculation must be made on the same side; therefore, an uneven number of swings are observed. The observation of $3 + 2$ or $4 + 3$ turning points is sufficient for accurate weighing; the resting point in this case is determined to the second decimal place. It frequently happens that the position of the resting point changes, especially after the weighing of heavy loads.

Suppose the resting point to be 9.53 on the scale, then in the process of weighing it is unnecessary to adjust the weights so that the second resting point will be exactly at the same position.

Assuming, when the weighing is made to one centigram, the weight $= 10.28$ gm., let the rider be placed at 5 mg., and suppose the resting point then to be 9.20. Let the rider be next placed at 6 mg., and suppose the resting point to be 10.16. Then 1 mg. corresponds to 0.96 scale divisions, and hence 10.285 gm. are too light by an amount which corresponds to $9.53 - 9.20 = 0.33$ scale divisions, *i.e.*, $\frac{0.33}{0.96} = 0.34$ mg. The true weight therefore is equal to 10.28534 g.

It is even unnecessary to make this double adjustment of the rider. Apart from the determination of the resting point, a single observation near the correct weight will suffice when the operator has once constructed a sensibility table.

By the sensibility of a balance is meant the deviation in scale divisions produced by an increase of 1 mg. in the load. The amount of deviation is always more or less dependent on the load.

For different loads the balance is adjusted with equal weights in each pan. A small excess of *a* mg. is then placed in the one pan.

The resting point is thereby removed n scale divisions, and the sensibility for the given load is $\frac{n}{a}$. When this value has been determined for loads of 5 : 5 or 10 : 10 gm. and a curve constructed with the loads as abscissas and the corresponding sensibilities as ordinates, the operator can, with the help of this curve, easily make the necessary correction for any weighing which is approximately correct.

Relative and Absolute Weighing.—The chemical balance is generally employed to determine relative and not absolute weights. This being the case, a slight inequality in the lengths of the arms can be neglected if the weights are always placed upon the same pan.

On the other hand, if the absolute weight is to be determined, it is desirable to know the ratio of the lengths of the two arms. This is found by the method of double weighings. If p represents the weight of the load q placed upon the left pan of the balance, and p_1 the weight of the same load placed upon the right pan, then the ratio of the lengths l and r of the left and right arms is found from the simple equation of the lever:

$$q\,l = p\,r \text{ and } p_1\,l = q\,r;\ \frac{r}{l} = \sqrt{\frac{p_1}{p}}.$$

The weight of a load obtained by placing the weights on the right pan of the balance must be multiplied by the above ratio in order to obtain the absolute weight.

The absolute weight can also be determined from a double weighing without a knowledge of the ratio $\frac{r}{l}$.

From the equations $q\,l = p\,r$ and $p_1 l = q\,r$, we have $q = \sqrt{p\,p_1}$; or, simplified $= \frac{1}{2}\,(p + p_1)$*,—*i. e.*, the true weight of the load q is the arithmetic mean of the weighings on the right and left pans of the balance.

The tare method is also applicable. The load q is brought into equilibrium with a second set of weights, or another load, and then instead of q is placed enough weights to bring the balance again into equilibrium.

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* Kohlrausch, Prakt. Phys. VII, 35, 1892.

Reduction of Weighings to a Vacuum Standard.—When brass weights (density $= 8.4$) are used, this reduction is made according to the formula,—

$$P = p\left[1 + 0.0012\left(\frac{1}{d} - 0.12\right)\right];\ *$$

where P represents the weight of the substance *in vacuo*, p is the apparent weight obtained by weighing in air, and d is the density of the weighed substance.

The error introduced by neglecting this reduction to a vacuum standard is greater, the greater the difference between the specific gravity of the weighed substance and that of the weights. Even for relative weighings in chemical analysis, where it is unnecessary to determine the absolute weight, this reduction is too often neglected.

Calibration of a Set of Weights and Preparation of a Correction Table.—Let the larger weights of the set be designated as $50'$, $20'$, $10'$, $10''$, $5'$, $2'$, $1'$, $1''$, $1'''$, and let the arms of the balance be of unequal length.

In this case, by the method of double weighings of the weights against each other, suppose we have,—

LEFT		RIGHT.
$50'$	correspond to	$20' + 10' + 10'' + \ldots a$ mg.
$20' + 10' + 10'' + \ldots b$ mg.	correspond to	$50'$.

Then according to page 11:

$$50' = 20' + 10' + 10'' + \ldots \tfrac{1}{2}(a + b) \text{ mg.}$$

In the same manner we obtain

$$20' = 10' + 10'' + \tfrac{1}{2}(c + d);$$
$$10'' = 10' + \tfrac{1}{2}(e + f), \text{ etc., etc.}$$

Representing the corrections $\frac{1}{2}(a + b)$, $\frac{1}{2}(c + d)$, $\frac{1}{2}(e + f)$, . . . by α, β, γ, . . . we have the following relations:

$$\begin{aligned} 50' &= 20' + 10' + 10'' + \ldots \alpha \\ 20' &= 10' + 10'' + \ldots \beta \\ 10'' &= 10' + \ldots \gamma \\ 5' + 2' + 1' + 1'' + 1''' &= 10' + \ldots \delta, \end{aligned}$$

in which α, β, γ, and δ can be positive or negative.

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* Kohlrausch, Prakt. Phys. VII, 36, 1892, and Landolt-Börnstein, p. 4, 1883, Tables.

Comparing all the weights against the $10'$ gm. weight, we have,—

$$\begin{aligned}
50' &= 5 \times 10' + \alpha + \beta + 2\gamma + \delta \\
20' &= 2 \times 10' + \beta + \gamma \\
10'' &= 1 \times 10' + \gamma \\
10' &= 1 \times 10' \\
5' + 2' + 1' + 1'' + 1''' &= 1 \times 10' + \delta \\
\hline
S = 50' + 20' + 10' + 10'' + 5' + 2' + 1' + 1'' + 1''' &= 10 \times 10' + (\alpha + 2\beta + 4\gamma + 2\delta).
\end{aligned}$$

If the correction table is to be drawn up with reference to the standard gram, one of the weights must be compared with a standard weight. For most work in chemistry (analysis, specific gravity determinations, etc.) this is not necessary.

In such cases the corrections for the single weights are assumed to be so small that the sum S of the larger weights is correct; then $S = 10 \times 10' + (\alpha + 2\beta + 4\gamma + 2\delta) = 100$ gm.

Let $\frac{1}{10}(\alpha + 2\beta + 4\gamma + 2\delta) = \sigma$, then

$$\begin{aligned}
10' &= 10 \text{ g.} - \sigma \\
10'' &= 10 \text{ "} - \sigma + \gamma \\
5' + 2' + 1' + 1'' + 1''' &= 10 \text{ "} - \sigma + \delta \\
20' &= 20 \text{ "} - 2\sigma + \beta + \gamma \\
50' &= 50 \text{ "} - 5\sigma + \alpha + \beta + 2\gamma + \delta.
\end{aligned}$$

In a similar manner the five weights $5'$, $2'$, $1'$, $1''$, and $1'''$ are compared with each other, and likewise the smaller weights. For the latter, however, a single weighing is sufficient, even though the balance-arms are of unequal length. If the balance-arms are equal, a single weighing is sufficient for any of the weights.

II. DENSITY (SPECIFIC GRAVITY).

General.—The density of a body is the mass of unit volume. For solid and liquid bodies the mass of 1 c.c. of water at 4° is considered the unit of mass. The density, then, of a body may be defined as the ratio of its mass to the mass of an equal volume of water at 4°.

The specific gravity of a body is the weight of unit volume. As the ratio of the weights of bodies in a vacuum is the same as the ratio of their masses, the numerical value of the density and specific gravity is the same.

The densities of gases are usually spoken of as vapor densities. The vapor density of a gas is the ratio of the mass of unit volume of the gas to the mass of unit volume of a standard gas at the same temperature and pressure. Dry air is usually taken as the standard gas.

By specific volume is meant the reciprocal of the specific gravity,—the volume of unit mass.

The atomic and molecular volumes are the volumes which the weights corresponding to the atomic and molecular weights occupy.

Let p represent a given weight of substance in grams, v the volume in cubic centimeters, d and s the density and specific gravity, φ the specific volume, a and m the atomic and molecular weights, v_a and v_m the atomic and molecular volumes, then from the above definitions we have the following relations:

$$d = s = \frac{p}{v};\ \varphi = \frac{1}{d} = \frac{v}{p};\ v_a = a\,\varphi = \frac{a}{d} \text{ and } v_m = \frac{m}{d}.$$

1. DENSITY OF SOLIDS.

(*a*) The Pyknometer.

Principle and Calculation.—The pyknometers represented in figures 1 and 2 are usually employed.

The pyknometer is weighed, filled (1) with air, (2) with water, and (3) with water plus the substance to be investigated.

Let the weight of substance taken be represented by p_s, the weight of the water required to fill the pyknometer at the temperature t by p_w = [(pyknometer + water) — (pyknometer + air)], and the weight of the substance and water in pyknometer by p_{ws} = [(pyknometer + water + substance) — (pyknometer + air)], then the uncorrected specific gravity

$$= \frac{p_s}{p_s + p_w - p_{ws}}$$

Reducing this to a vacuum standard and to the temperature 4°, the specific gravity s becomes

$$s = \frac{p_s}{p_s + p_w - p_{ws}} (Q - \lambda) + \lambda.*$$

Q represents the specific gravity of water at the ordinary temperature t, † and $\lambda = 0.0012$, the average density of the air compared with water at 4°.

If the temperature at the time of weighing the water is different from that at the time of weighing the water plus the substance, a correction must be introduced for the expansion of the water and glass; and the formula becomes

$$s = \frac{p_s\ (Q - \lambda)}{p_s + p_w - p_{ws} + p_w\ [Q - Q_w + 3\,\beta\,(t - t_w)]} + \lambda.‡$$

t and Q represent the temperature and specific gravity of water at the time of weighing the water plus the substance, t_w and Q_w represent the corresponding values at the time of weighing the water alone, and $3\,\beta$ is the coefficient of cubical expansion of glass $= 0.000025$ (for Jena glass $= 0.0000237$).

For substances which are soluble in water other liquids are used,—alcohol, benzene, petroleum, turpentine, etc. In such cases the above expression must be multiplied by the specific gravity of the liquid employed.

Method of Operation.—The pyknometer (Fig. 1) consists of a glass vessel A and a ground-glass stopper b, through which passes a capillary tube. When the pyknometer is filled with the liquid, the cork is inserted in such a manner that no air-bubbles remain in the flask, and so that the liquid rises to the top of the capillary opening or to a definite mark on the cork.

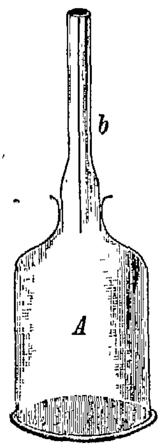

FIG. 1.

A more complete pyknometer is represented in figure 2. The

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* Kohlrausch, Prakt. Phys. VII, 47, 1892.

† Landolt-Börnstein, Tables, pp. 33–35, 1883.

‡ Kohlrausch, Prakt. Phys. VII, 49, 1892; also Graham-Otto, III, 1. Abt., p. 371.

thermometer inserted through the neck *h*. of the vessel *A* is graduated to $\frac{1}{5}°$. When the vessel is filled with liquid the air-bubbles are completely removed and a portion of the liquid is removed from the small tube *c* by means of filter-paper, until the surface of the liquid just reaches the top of the mark *m*. The tube *c* is closed with a small stopper.

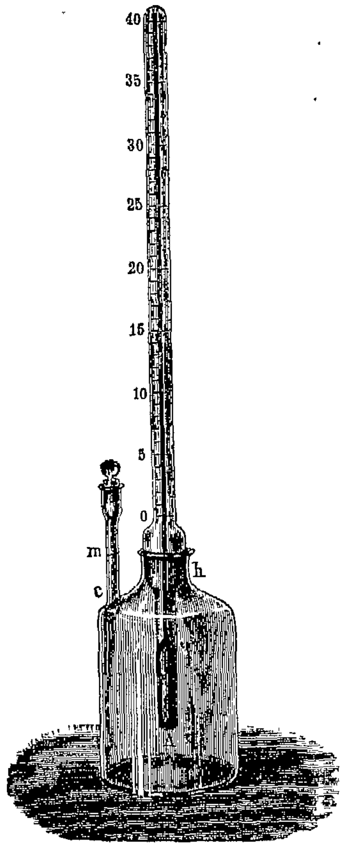

FIG. 2.

The pyknometer is next dried by means of alcohol and ether, and weighed; it is then filled with boiled water and reweighed, the temperature being noted at the same time. From these two weighings the weight of the water p_w is calculated. Finally, the substance is weighed, either in or outside of the pyknometer, and its weight represented by p_s. The value p_{ws} is then determined by weighing the pyknometer containing the substance and water. The pyknometer can be previously brought to a constant temperature in a water-bath when the observations can not be made at the temperature of the room. After inserting the stopper or thermometer the pyknometer is carefully dried by means of filter-paper and a piece of silk; heating must be avoided. If the substance whose specific gravity is to be determined is too light, it is made to sink in the liquid by placing it in a vessel made of glass, metal, or wire net, which remains in the pyknometer during all the weighings.

The pyknometric method gives far less accurate results for solids than for liquids. Greater errors can be introduced for pulverized substances by the absorption of air at the surface, and for crystals

or minerals by the inclosure of air or the mother-liquor, or by other heterogeneities.

Great care is therefore necessary in the selection of the substance; a previous microscopic examination is sometimes necessary. The adhering air can often be removed by shaking or frequently immersing the substance, or even wetting it with a brush.

In the investigation of pulverized substances the pyknometer, when filled, is placed under an air-pump and exhausted so far that bubbles of air no longer rise in the liquid. It is still better to boil the liquid while under the air-pump. For this purpose use is made of a simple apparatus described by von Petersen (Zeitschr. physik. Chem. 8, 602, 1890). If the homogeneity of a crystal is uncertain, it is better to powder it for pyknometric observations.

The removal of the inclosed air or mother-liquor by heat is not to be recommended, as the density in such processes frequently undergoes a change.

(*b*) The Method of Floating Crystals.

This method * in many cases is capable of greater accuracy than the pyknometric method, and a smaller quantity of substance is necessary for its execution.

For reasons given on page 16, the pyknometric method, even for apparently homogeneous, well-formed crystals, is sometimes accompanied by such errors that the determinations of the specific gravity show a variation of several units in the second and even in the first decimal place.

A microscopic separation of the crystals would in most cases be a waste of time.

On the other hand, homogeneous crystal fragments free from inclosures are easily obtained by the following method:

A small, separatory funnel is half filled with a liquid of rather high specific gravity. For most crystallized substances methylene iodide (specific gravity = 3.3) is used. Suppose the specific gravity of the crystals under investigation to be less than 3.3, then the crystals which are placed in the separatory funnel will float on the

* Retgers, Zeitschr. physik. Chem. 3, 289 and 298, 1889; 9, 328, 1883.

liquid. A liquid of low specific gravity, as benzene, is allowed to drop into the first liquid until a point is reached where the specific gravity of the liquid is equal to or less than that of the crystals. The crystals then begin to sink into the liquid. Those crystals which inclose either none or the smallest quantity of mother-liquor and air will sink first.

When the sunken crystals are examined under a microscope they are found to consist mostly of single, and often very small, crystal fragments, which prove to be so pure and homogeneous that they can be used in the investigation.

The determination is carried out in the following manner, according to the principle already developed.

The separatory funnel is again filled with methylene iodide and one of the purest crystal fragments placed upon the surface of the liquid. Benzene is added until the crystal just floats in the middle of the liquid. The specific gravity then, of the liquid mixture, is equal to that of the crystal. If a small pyknometer (Fig. 2) be placed under the separatory funnel and filled with the liquid mixture as quickly as possible to prevent any change in the concentration, the specific gravity of this liquid is the same as that of the crystallized substance.

As it is difficult to adjust the conditions so that the crystal will float exactly in the middle of the liquid, it is better to conduct the experiment so that (1) the crystal slowly sinks, (2) slowly rises, and (3) approximately floats. The three values thus obtained for the specific gravity must agree within one unit in the third decimal place. Heating should be avoided in drying the pyknometer, as a difference of 1° in temperature changes the specific gravity of methylene iodide about 0.002. The observation temperature should always be noted.

If the substance under investigation is heavier than methylene iodide, it is made to float by attaching to it a glass or platinum shell.*

The method, however, in such cases is not to be recommended.

The rather costly methylene iodide (100 gm. = $2.50) is separated from the benzene by simple evaporation or fractionation; the

* Retgers, Zeitschr. physik. Chem. 4, 189, 1889.

crystals are freed from methylene iodide by washing with benzene until the red color disappears.

Potassium sulphate or sodium chloride, the specific gravities of which were shown by Retgers to be 2.666 (at 20°) and 2.167 (at 17°), are well adapted to this or the pyknometric method.

It is sufficient to carry the determinations of the specific gravities of solids to the third or at most to the fourth decimal place; the fourth decimal is always unreliable.

The floating method is also applicable for the investigation of minerals. For this purpose, as well as for insoluble artificial crystals, use is made of Thoulet's solution,—*i. e.*, an aqueous solution of potassium mercuric iodide,—in which the mineral fragments are made to float by diluting the solution with water, stirring well at the same time (Goldschmidt, Neues Jahrb. für Mineral., Beil. Bd. I, p. 179; also Rosenbusch, Mikrosk. Physiogr. der Mineralien, sec. 231, 1892, and Retgers, Zeitschr. physik. Chem. 4, p. 189, 1889).

For other methods of determining the specific gravity of solids, see the application of the hydrostatic balance (Retgers, Zeitschr. physik. Chem. 3, p. 301, 1889). The volumenometer is applicable, especially for powdered substances. (Wiedemann and Ebert, Phys. Prakt., p. 79, 1890, and Kohlrausch, Prakt. Phys. VII, p. 50, 1892. Tables of the Specific Gravities of Solids, Landolt-Börnstein, Physik. Chem., p. 78, 1883.)

2. DENSITY OF LIQUIDS.*

(*a*) THE PYKNOMETER.

Principle and Calculation.—A suitable glass vessel is weighed, filled (1) with air, (2) with water, (3) with the liquid under investigation.

The apparent weight of the liquid in air is represented by $p_s =$ [(pyknometer + liquid) — (pyknometer + air)]. The weight of an equal volume of water by $p_w =$ [(pyknometer + water) —

* [Kohlrausch and Hallwachs have recently introduced a very accurate method for determining the density of solutions, Wied. Ann. 53, p. 14, 1894.—Tr.]

(pyknometer + air)]. The uncorrected specific gravity then is $\frac{p_s}{p_w}$. Reduced to water at 4° and to a vacuum standard this becomes

$$s = \frac{p_s}{p_w}(Q - \lambda) + \lambda,^*$$

where Q = the density of water at the observation temperature t and $\lambda = 0.0012$ = the average density of the air compared with water. As Q is usually very slightly less than unity, it is often

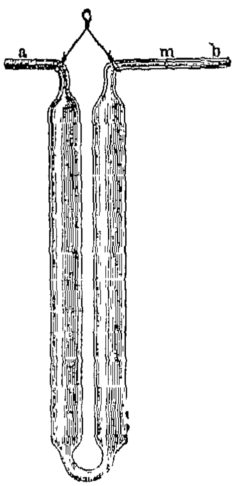

FIG. 3.

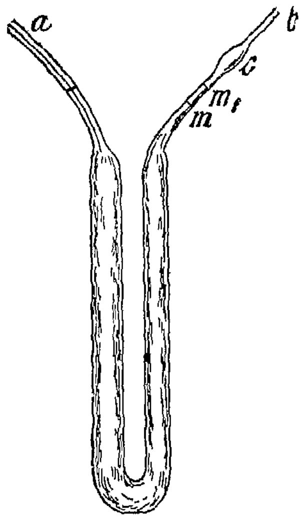

FIG. 4.

convenient to substitute $Q = 1 - \delta$ in the formula, whence we have:

$$s = \frac{p_s}{p_w} - (\delta + \lambda)\frac{p_s}{p_w} + \lambda.$$

If the specific gravity of the liquid is determined at a temperature different from that at which the water content is determined, the specific gravity is then calculated from the formula:

$$s = \frac{p_s}{p_w}[1 + 3\beta(t_w - t)](Q - \lambda) + \lambda;$$

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* Kohlrausch, Prakt. Phys. VII, p 47, 1892.

t_w and t represent the temperatures of the water and the liquid at the time of weighing. $3\beta = 0.000025$ = coefficient of the cubical expansion of glass.

If the specific gravity determination is to be made as accurately as possible to the fifth decimal place, then λ is placed equal to 0.00119, and the coefficient of expansion of glass is determined

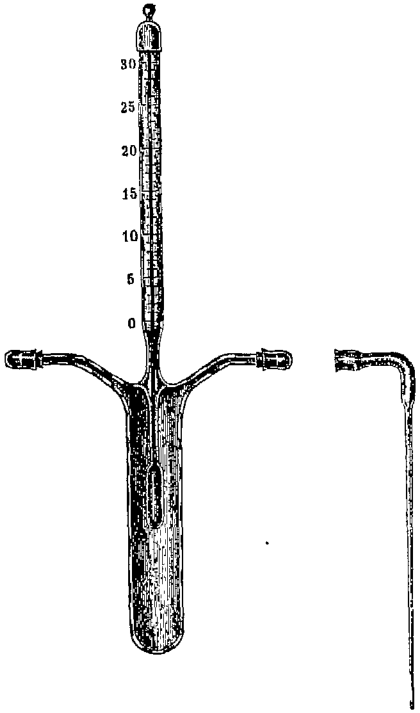

FIG. 5.

according to page 69, also the formulæ of Winkelmann, Graham-Otto, 3. Aufl., 1. Abt., page 371.

Method of Operation.—Leaving out viscous liquids, for which a pyknometer of the form represented in figure 2, page 16, with a wider tube is used,* more accurate determinations are made

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* Such a pyknometer is described by Brühl and Scheibler, Ber. d. d. chem. Ges. 24, pp. 182 and 357, 1891.

by using a Sprengel pyknometer, the most common forms of which are represented in figure 3 and figure 5.

In figure 3 is represented a U-shaped glass tube, which terminates at the top in two small horizontal tubes. A platinum wire is arranged in the middle for hanging the vessel to the balance. Tube *a* is smaller than tube *b*; at *m* on the tube *b* is a mark. Both tubes in this as well as in figure 5 can be closed with small glass caps, thereby preventing evaporation during the weighing. The pyknometer (Fig. 5) differs essentially only in that through the top of the tube is fused a thermometer graduated to $\frac{1}{5}°$ or $\frac{1}{10}°$, which must be carefully adjusted. Figure 4 represents a pyknometer * which possesses certain advantages for determining the specific gravity of highly volatile or expansible liquids, and also for investigations made at temperatures lower than that of the room.

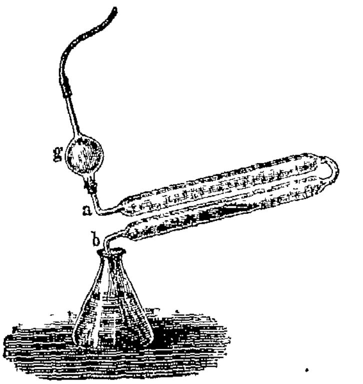

FIG. 6.

The wider capillary tube *b* is provided with a globular enlargement *c*, the capacity of which is so large that it will suffice even for highly expansible liquids.

The tubes are closed by means of rubber or glass caps.

The pyknometer is usually of from 5 to 20 c.c. capacity. When there is sufficient liquid for the investigation, the capacity is chosen with reference to the greatest accuracy of results.

The pyknometer is dried by means of alcohol and anhydrous ether. The filling is accomplished either by means of the mouth or a caoutchouc pipette as represented in figure 6, where the smaller tube *a* is connected to a glass globe *g* by means of a small cork, or finally with the help of a knee-tube (Fig. 5) which is slipped onto the larger tube *b* and immersed in the liquid. The

* Perkin, Jour. prakt. Chem., N. F. 31, p. 486, 1885.

filling must proceed in such a manner that all the air-bubbles are removed from the apparatus.

When completely filled, the pyknometer is placed or hung in a water-bath (or thermostat), so that only the upper tubes are free from the water, and indeed for the pyknometer figure 4, so that the wider tube *b* is in a vertical position.

If the specific gravity determination is to be made accurately to the fourth decimal place, the temperature of the water-bath must be kept constant to within 0.2°. For that reason a large water-bath is used, and to it is fastened a thermometer graduated to $\frac{1}{10}$°, when necessary, very near the pyknometer. For a complete equalizing of temperature, eight to ten minutes are necessary.

The quantity of liquid in the pyknometer, while in the water-bath, is so regulated that the smaller tube *a* is completely filled, and the tube *b* filled to the mark *m*. If the tube *b* contains too much liquid a small piece of filter-paper is brought to the end of the smaller tube *a*, and by carefully manipulating the same, the quantity of liquid can be adjusted so that it fills the tube *b* exactly to the mark *m*. If the quantity of liquid in the tube is too small, or if the filter-paper has removed too much liquid, then a glass rod with a drop of the liquid on the lower end is brought to the filled tube *a*. The amount of liquid in *b* increases immediately. When the quantity of liquid is properly adjusted the tubes *a* and *b* are carefully wiped with filter-paper and a piece of silk, to remove the liquid on the outside. The small glass caps are next placed on the tubes *a* and *b*, and the apparatus, after removing from the water-bath, is carefully dried, heating from the hand being carefully avoided. In no case should the liquid, from expansion by heat, be allowed to enter the small caps.

With the pyknometer figure 4 the liquid, after being adjusted to the mark *m*, is allowed to run back in *a* until the liquid in *b* stands at the mark m_1.

The water and other liquids, before the operation, are as far as possible freed from the dissolved air by boiling; the water used in preparing solutions must also be boiled, preferably after the preparation of the solution.

The determination of specific gravities at higher temperatures can be made according to the method of Ramsay-L. Meyer, page 28, or according to the method of Schiff.

The relation of the density of solutions to the percentage content see, among others, Gerlach, Specific Gravities of Salt Solutions, Freiberg, 1859, and Bremer, Zeitschr. phys. Chem. 3, page 425, 1889. Tables of Specific Gravities of Liquids, Landolt-Börnstein, Phys. Chem. page 88; of salt solutions, Gerlach, Fresenius, Zeitschr. anal. Chem. 8, page 279, 1869; 27, page 271, 1888, and 28, page 466, 1889.

(*b*) THE MOHR-WESTPHAL BALANCE.

It frequently happens that one wishes to make an approximate specific gravity determination quicker than is possible by the time-consuming pyknometric method. In this case use is made of either a Mohr-Westphal balance or of the aräometric method, page 27.

The Mohr-Westphal balance (Fig. 7) is supplied with a screw P for lengthening and shortening the stand, and a balance-beam which rests on the sharp edge at H. On one end of the beam is hung a glass float with a thermometer, while on the other end is a weight K which is really an enlargement of the beam. By proper adjustment of the foot-screw S of the stand, the weight K can be made to just balance the glass float in the air. The proper adjustment is shown when the two points J and K are exactly opposite each other. Sometimes a vertical scale is placed at J and the point K brought to the middle division

The balance-beam between the point where the thermometer is suspended and the point of support is divided into ten equal parts. The balance is provided with three and often four riders, $A_1 = A$, B and C, the weights of which stand in the ratio 1 : 10 : 100.

If, after the balance has been carefully adjusted in the air, the glass float be sunk into water and then into some other liquid, it is evident that equal volumes of the water and liquid will be displaced, and the equilibrium of the balance will be disturbed. To restore this equilibrium, sufficient weight must be placed on the beam in each case to exactly counterbalance the weight of the displaced liquid. The ratio of the weight of the liquid to that of the water represents roughly the specific gravity of the liquid.

The weights $A_1 = A$ are of such magnitude that when one is hung on the end of the beam, its weight exactly counterbalances the weight of the water at 15°, displaced by the glass float; hence when the balance is adjusted in the air and the glass body placed

in water at 15°, and the rider A_1 hung on the end of the beam, the balance is again brought into equilibrium with the points exactly opposite each other. The weight therefore is represented as $A_1 = A = 1$; likewise the weights of B and C hung at the same point on the beam would be 0.1 and 0.01, and accord-

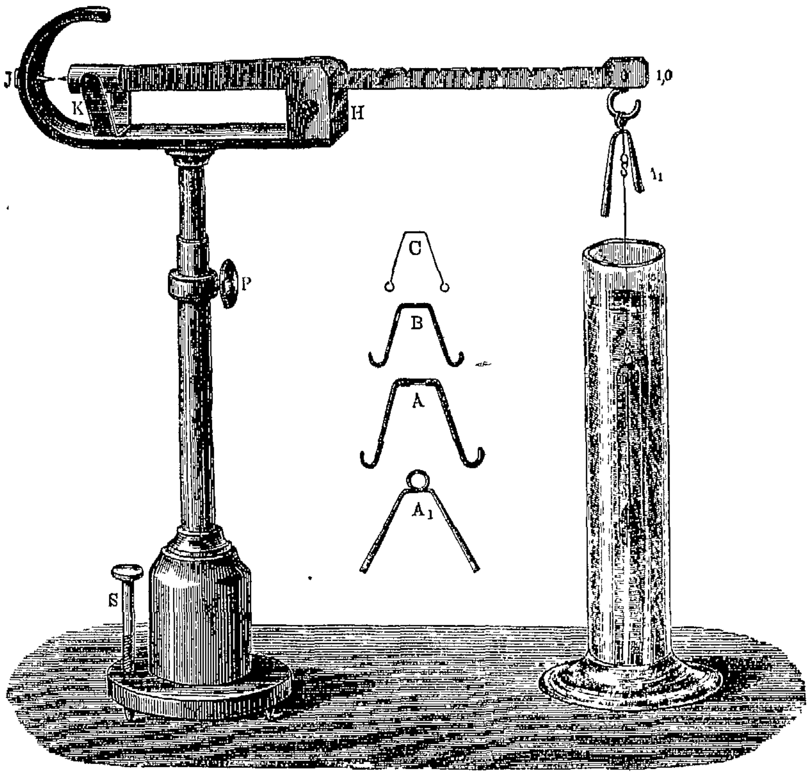

FIG. 7.

ing to the known laws of the lever, each of these weights in the divisions 9, 8, 7. . . . of the beam would be .9, .8, .7. . . . of the original weight. If therefore, the glass float, after being adjusted in the air and water, is sunk into the liquid to be investigated, it is only necessary for obtaining the specific gravity to determine what positions of the riders produce equilibrium in the balance. The

position of A gives the first, B the second, and C the third decimal place in the specific gravity. A_1 is used only when the specific gravity of the liquid is greater than unity. As an example, the positions of the riders in figure 8 and figure 9 represent the specific gravities 0.747 and 1.846 respectively.

With the better class of instruments determinations can be made to within about two units in the fourth decimal place. This degree of accuracy, however, requires a careful construction of the balance.

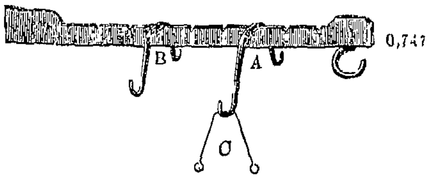

FIG. 8.

The distance between the divisions on the beam must be larger and the weights must stand exactly in the ratio given. The adjustment in air and water must never be omitted. If the adjustment for water is not perfect when A_1 is hung at the tenth division of the beam, the final adjustment must be made with the help of the other weights.

If the weight is 0.992 instead of 1, then all the readings of the balance are incorrect and must be divided by 0.992. The sensi-

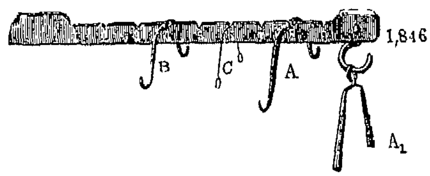

FIG. 9.

bility of the balance is sometimes lowered by the collection of rust and dirt on the knife edge on which the beam rests. This can be detected by readjusting the points of the balance after moving the beam with the hand; the position of the points should be the same when the balance comes to rest.*

* According to an article published by Kohlrausch and Hallwachs (Nachrichten Ges. Wiss., Gottingen, p. 350, 1893) the method of hydrostatic weighing is capable of great accuracy, being possible to determine the specific gravity to the sixth decimal place.

(*c*) THE ARAOMETER.

The aräometer consists of a glass stem weighted usually with mercury; the more accurate instruments are provided with a thermometer. The instrument is placed in the liquid to be examined, into which it sinks to a definite mark on the stem.

The same instrument will stand at different positions in different liquids depending upon their specific gravities.

The aräometer is sunk into liquids of known specific gravities; the stem is marked in each case at the surface of the liquid and provided with an empyrical scale which represents the specific gravities. The instrument can then be used for liquids of unknown densities. When the determination is to be made with greater accuracy the temperature is taken into account, and the reading should be made so as to exclude any error due to parallax.

Sometimes the apparatus is used to determine the percentage content of certain solutions or mixtures, and is then called alcoholometer, saccharimeter, etc. The scale gives directly in these cases the percentage of alcohol, sugar, etc.

The aräometric method, with good instruments, is capable of an accuracy which is but slightly inferior to the pyknometric method.

It has recently been shown that the heretofore neglected influence of the surface tension, which is different for different liquids, at the place where the stem comes in contact with the surface of the liquid, produces an error of from two to four units in the third decimal place. The same aräometer then is not applicable, as was previously supposed, for liquids of different surface tension, but only for a single liquid, or by using a correction table for a group of liquids with nearly equal surface tensions. Such aräometers for definite liquids are constructed by the physico-technical Reichsanstalt, and are supplied with the necessary tables. These are at present in the market, and are capable of an accuracy of one unit in the fifth decimal place in the specific gravity.*

* Fock, Zeitschr. physik. Chem. 2, p 296, 1888, and Weinstein, *ibid.* 7, p. 79, 1891.

(*d*) DETERMINATION OF THE SPECIFIC GRAVITY AT HIGHER TEMPERATURES AS WELL AS THE MOLECULAR VOLUME OF LIQUIDS AT THEIR BOILING POINTS.

METHOD OF RAMSAY-LOTHAR MEYER.*

Principle and Calculation.—The specific gravity and molecular volume of a liquid at the boiling point is determined by this method, in which a pyknometer (Fig. 10) is filled with the liquid and heated to the boiling point in the vapor of the same liquid in a boiling-vessel.

FIG. 10.

As the volume of the pyknometer changes with the temperature, the coefficient of the cubical expansion of glass must be known. If the pyknometer is made of Jena standard glass (No. 14), then, according to Weidmann,† $3\beta = 0.0000237$. The value of 3β can be determined in the manner described on page 75.

The pyknometer is next weighed filled with air and then with distilled water at two temperatures, t and t_1, rather far apart, about the temperature of the room and the boiling point of water; then from page 14 we have:

$$v_t = \frac{p_t}{s_t} \text{ and } v_{t_1} = \frac{p_{t_1}}{s_{t_1}},$$

where v, p, and s represent the volume, weight, and specific gravity of water at the temperatures given;
therefore:

$$v_{t_1} - v_t = \frac{p_{t_1}}{s_{t_1}} - \frac{p_t}{s_t} \text{ and } 3\beta = \frac{v_{t_1} - v_t}{t_1 - t} = \frac{\frac{p_{t_1}}{s_{t_1}} - \frac{p_t}{s_t}}{t_1 - t}.$$

For the specific gravity of water at different temperatures see Landolt-Börnstein's Tables, pp. 34–36, 1883.

If 3β is known, the volume for any given boiling point ϑ between t and t_1 is:

$$v_\vartheta = v_t + 3\beta(\vartheta - t) = \frac{p_t}{s_t} + 3\beta(\vartheta - t),$$

* Neubeck, Zeitschr. physik. Chem. 1, p. 651, 1887, and Feitler, *ibid.* 4, p. 66, 1889.

† Weidmann, Inaug. Dissert., Jena, 1886

p_t is the weight and s_t the specific gravity of the water in the pyknometer at t°. By making a larger number of determinations the corresponding volumes for temperatures between t and t_1 can be calculated according to the above formula.

If ϑ represents the boiling point of the substance to be investigated, then the specific gravity at that temperature is $s_\vartheta = \frac{p_\vartheta}{v_\vartheta}$, where p_ϑ is the weight of the liquid at the boiling point [(pyk. + liq.) — (pyk. + air)], and v_ϑ is the volume of pyknometer at the temperature ϑ. Then the molecular volume $v_m = \frac{m}{s_\vartheta}$, where m represents the molecular weight of the substance. The reduction of the weighings to a vacuum standard can here be omitted. For molecular weights see table at end of this volume.

Apparatus and Method of Operation.—The pyknometer (Fig. 10) of about 2.5 c.c. capacity consists of thin glass (Jena standard glass, No. 14).

The wider, closed cylindrical part is united with a somewhat longer, rather narrow capillary tube with a turned-up point.

The filling of this pyknometer with a liquid can be accomplished with the help of the apparatus shown in figure 11.

A wide tube closed with a rubber stopper is connected through a side tube with an exhaust pump and the outer air by means of two stop-cocks. The air, before entering from the outside, must pass through a calcium chloride tube.

The bottom of the tube is filled with the liquid, into which the pyknometer is sunk by means of a wire which passes air-tight through the rubber stopper. The pyknometer is lowered into the vessel until the point of the capillary tube is immersed in the liquid. By repeated opening and closing of the pump and letting in air, it is an easy matter to fill the pyknometer with liquid, with the exception of a small air-bubble which, upon subsequent heating, disappears. Simultaneous heating of the liquid and apparatus hastens the filling.

The subsequent emptying of the pyknometer is accomplished in the same apparatus. The pyknometer is hung with the point upward, and the two stop-cocks alternately opened and closed. It is then dried by means of alcohol and anhydrous ether.

The almost filled vessel is hung in the boiling-flask * represented in figure 12, by means of a nickel wire γ which passes air-tight through the cork k.

The rather wide boiling-flask, in which the liquid in the pyknometer is allowed to boil, is connected with a reflux condenser, which in turn can be connected with a Städel-Hahn or some other form of pressure regulator. With this arrangement the liquid can be made to boil under increased or diminished pressure. The method permits then of a determination of the specific gravity and molecular volume at different pressures and temperatures. By means of the regulators mentioned, the pressure can be measured accurately to within about 2 mm.

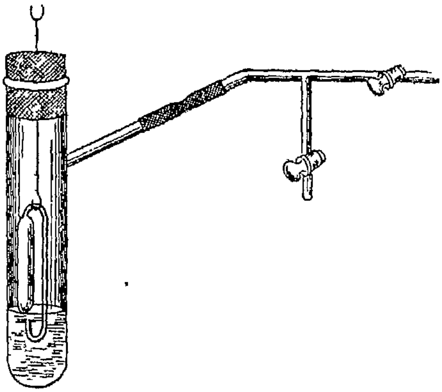

FIG 11.

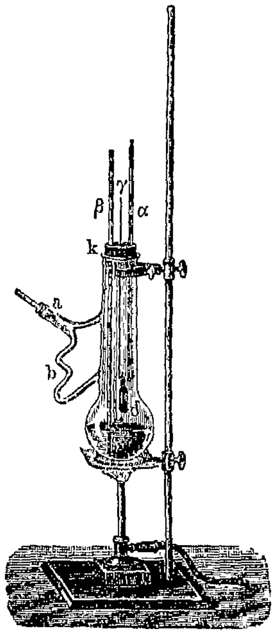

FIG. 12.

The thermometer α fastened in the cork must be tested and adjusted as described under Section xx.

For liquids which cause bumping, it is advantageous to have a capillary tube β passing through the stopper to the bottom of the flask, through which a current of air or carbon dioxide is passed.

* Of course, the filling and emptying of the pyknometer can also be accomplished in this flask; however, it is less convenient.

The pyknometer filled completely, with the exception of a small air-bubble, is hung in the flask so that the point of the capillary tube remains in the vapor. The desired pressure is then obtained and the liquid in the boiling-flask brought to boiling. The liquid in the pyknometer expands and drops out of the capillary tube, taking with it the last trace of air, until it has assumed the constant temperature equal to that of the boiling point of the liquid.

The boiling is then stopped. The liquid in the pyknometer cools and draws back through the capillary tube, with the exception of a small drop which hangs on the end of the tube; the vessel is then dried and weighed.

If the substance becomes stiff on cooling, the pyknometer may break. This danger can be avoided by repeatedly melting the outer layer, thereby distributing the mass uniformly, or by weighing before the complete stiffening of the substance. Substances for investigation, see Neubeck, Zeitschr. physik. Chem. 1, p. 651, 1887.

A second method which is to be recommended for determining molecular volumes is that of R. Schiff (see p. 76).

Literature on Molecular Volumes.—Ostwald, Allgemeine Chemie, 2. Aufl., Bd. 1, pp. 357 and 838; R Schiff, Lieb Ann. 220, pp 71 and 278, also Ber. d. d. chem. Ges. 14, p. 2761, 1881; Ramsay, Jour. Chem. Soc. 35, p. 463, 1879; Thorpe, *ibid.* 37, pp. 141 and 327, 1880; Lossen and his students, Lieb. Ann. 214, p. 81; 221, p. 61; 224, p. 56; 225, p. 109; Gartenmeister, Inaug. Dissert., Königsberg, 1885, and Lieb. Ann. 233, p 249; Städel, Ber. d. d. chem. Ges. 15, p. 2559, 1882; Elsässer, Lieb Ann. 218, p 302, 1883; Vollmar, Ber. d. d. chem. Ges. 15, p 2560, 1882; Horstmann, *ibid.* 19, p. 1579, 1886, and 20, p. 766, 1887; Bartoli, Ann. chim phys. (6), ser. VII, p. 394, 1886; Kopp, Mémoires sur les vol. mol. des liquides (Winter, Heidelberg, 1886), and Lieb. Ann., 250, p. 1, 1889; Neubeck, Zeitschr. physik. Chem. 3, p. 649, 1889; Feitler, *ibid.* 4, p. 66, 1889; Lossen, 243, p. 64, and 254, p. 42, 1889; Groshans, Kosmos, 1891, Ref. Zeitschr. physik. Chem. 8, p. 431, 1891.

[See also the recent investigations of J. Traube, Zeit f anorg Chem. 3, p. 11, 1893, and 8, p. 12, 1895; Ber d d. chem. Ges. 28, p. 2924, 1895; 28, p. 3296, 1896; 30, p 273; and 33, p 130, 1898; Wied. Ann. 61, pp. 380 and 395, 1897.—Tr.]

(*e*) Contraction and Dilation.

By the contraction or dilation, produced in the mixing of liquids or the solutions of solids in liquids, is meant the change of volume per unit volume of the original substances.

If, for example, two liquids of volumes v_1 and v_2 are mixed and the volume of the mixture is v_3, then the volume change per unit volume is:

$$c = \frac{v_1 + v_2 - v_3}{v_1 + v_2}.$$

A contraction has taken place when c is positive, and a dilation when c is negative. From page 14 we have $v_3 \frac{p_3}{s_3}$, where p_3 and s_3 represent the weight and specific gravity of the mixture. p_3 is equal to $p_1 + p_2$, the weights of the original liquids, and these in turn are equal to $v_1 s_1 + v_2 s_2$. We have then the equation:

$$c = \frac{(v_1 + v_2) s_3 - (v_1 s_1 + v_2 s_2)}{(v_1 + v_2) s_3}.$$

For the determination of contraction or dilation according to this equation, it is only necessary to note the volumes v_1 and v_2 of the original liquids, and to determine, by known methods, their specific gravities s_1 and s_2, as well as the specific gravity s_3 of the mixture.

For solutions of solids the same formula holds good. On contraction of solutions, see Ostwald, Allgem. Chem., 2. Aufl., Bd. 1, p. 782 *et seq.*, 1891.

3. THE DENSITY OF GASES (Vapor Density).

(*a*) METHOD OF DUMAS.

Principle.—The weight of a given volume of a gas is determined, and then, according to the known laws of Boyle and Gay-Lussac, the vapor density is calculated, *i. e.*, the weight of unit volume of the gas compared with dry atmospheric air at the same temperature and pressure.

Apparatus and Method of Operation.—A thin-walled glass balloon of about 100 to 300 c.c. capacity, with a side tube (Fig. 13) is, after drying, drawn out at a into a smaller tube of about 1 mm. in diameter. Let the weight of the dry balloon be represented by p. While gently warming the balloon several grams of the liquid to be investigated are allowed to enter. The balloon is placed in a water-, oil- or paraffin-bath up to the narrowed part a.

The temperature of the bath is regulated so as to be at least 10° above the boiling point of the liquid at the end of the experiment. When the liquid in the balloon has been completely changed to vapor, there being enough of the substance present to expel all the air, the balloon is melted off at a by means of a blow-pipe flame, after which the barometric pressure b and the temperature t of the water-bath are observed. After cooling, the balloon, together with the melted-off glass tube, is weighed. Let this weight be represented by p_s; let the barometric pressure and the temperature at the time of weighing be b_1 and t_1. To test for the presence of air in the balloon, the point is then broken off under recently boiled water which is free from air. The balloon is filled completely with water only in cases where the previous removal of air had been complete.

If the filling with water is complete, the balloon together with the water and the melted-off glass tube is placed upon a balance and weighed to within one centigram. Let the weight be p_w and the temperature of the water again be t_1.

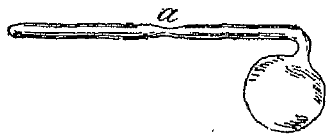

FIG. 13.

Calculation.—The weight of the empty balloon can be taken equal to p, since the quantity of air displaced by the thin-walled balloon is nearly the same as that present in the balloon at the time of weighing.

$p_w - p$ can be taken as the weight of the water at $t_1°$, since the weight of the air displaced by the balloon in comparison with the weight of the water can be neglected. If Q is the specific gravity of water at $t_1°$,* then the volume of the balloon is:

$$v_{t_1} = \frac{p_w - p}{Q}.$$

The volume v_t at the temperature of the water-bath may be calculated from v_{t_1} by the formula $v_t = t_1 + 3\,\beta\,(t - t_1)$, where $3\,\beta$ is the coefficient of cubical expansion of glass, and can be taken as 0.000025.

The weight g of the vapor contained in the balloon is found from

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* Landolt-Börnstein's Tables, pp. 33 and 34, 1883.

the expression $g = p_s - p + l$, where l is the weight of the air displaced by the balloon.

At the ordinary pressure b_1 and temperature t_1 we have:

$$l = \frac{v_{t_1} b_1 \, 0.001293}{76 (1 + a t)},$$

where v_{t_1} is the volume of the balloon at $t_1°$, 0.001293 is the weight of 1 c.c. of air at 0° and 76 cm. pressure, and a the coefficient of expansion of gases = 0.00366.

The vapor density d is then given by the formula:

$$d = \frac{g \, 76 \, (1 + a \, t)}{v_t \, b \, 0.001293},$$

and the molecular weight m is equal to 28.9 d.

It frequently happens in the vaporization of the substance that the air is not completely removed from the balloon, as can easily be seen from the subsequent filling of the vessel with water. If the error introduced in this manner is to be neglected, fill the balloon completely and calculate according to the above formula. Otherwise the balloon is sunk into the water after breaking off the point, until the inner and outer surfaces of the water stand at the same level. The balloon with this quantity of water is weighed and the weight represented by p_{wl}; it is then filled completely with water and again weighed; this weight $= p_w$. The calculation of the exact vapor density, taking into account all sources of error, follows from the equation:

$$d = \frac{(p_s - p) \dfrac{Q}{\lambda'} + p_{wl} - p_s}{(p_w - p) \dfrac{b}{b_1} \dfrac{1 + 0.00367 t_1}{1 + 0.00367 t} [1 + 3 \beta (t - t_1)] - (p_w - p_{wl})}.$$

λ' represents the density of the air at the temperature $t_1°$ and pressure b_1.*

(*b*) METHOD OF GAY-LUSSAC-A. W. HOFMANN.

Principle.—A quantity of substance weighed off in a small glass vessel is introduced into a barometer tube, the lower end of

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* Kohlrausch, Prakt. Phys. VII, 55; *ibid.* Table, p. 406, 1892.

which is immersed in mercury. This tube is surrounded by a glass jacket, which is heated to constant temperature by means of boiling vapors. Taking into account the pressure and temperature, the volume occupied by the vaporized substance is read off, and from this volume for a given weight of substance the vapor density is calculated.

Apparatus.—An accurately calibrated * wide barometer tube, *A* (Fig. 14), of about 76 cm. in length, is set upright in a mercury trough and fastened below in a wider glass jacket *B* by means of a cork. The jacket is heated by means of the vapors of boiling liquids (water, anilin, etc.), which are conducted in through the tube *a* and out through the tube *b*, and finally condensed in a coiled tube cooled with water.

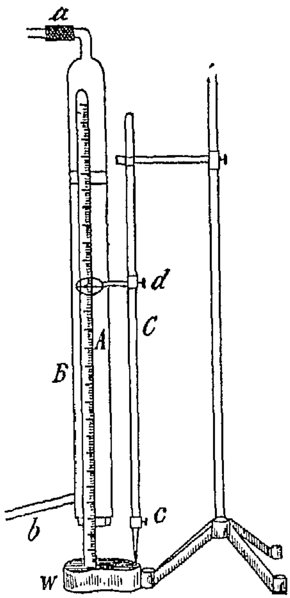

FIG. 14

The arrangement for reading off the volume of gas consists of a metallic, upright bar *C*. This is provided with a nut in which are fastened, in vertical positions, two metallic bars, one of which is graduated in millimeters; these can be raised or lowered by means of the screw *c*. The second bar ends in a point which forms the zero of the scale, and is lowered toward the surface of the mercury in the trough *w* until the point seems to touch its image formed by the reflection of the mercury, without actually coming in contact with the surface of the mercury. The height of the mercury in the barometer tube is determined by means of cross-wires in two vertical metallic rings, the height of which is so adjusted by means of the screw *d* that the two horizontal cross-wires and the top of the mercury are brought into the same plane.

* For method of calibration, see Wiedemann and Ebert, Phys. Prakt. 1, p. 99, 1890.

The height of the mercury in the barometer tube is given directly by the distance from the metallic point of the scale to the point where the screw d is situated on the same scale.

The substance is weighed in a small glass-stoppered flask (Fig. 15) which is placed on the balance in the small metallic or glass vessel represented in the figure.

Method of Operation.—The barometer tube A, cleaned and dried by means of alcohol, is filled with dry mercury free from air-bubbles. The air-bubbles clinging to the sides of the tube are removed by allowing the mercury to flow in and out several times. The tube, completely filled with mercury, is closed by means of the finger, inverted and placed upright in the mercury trough, so that a perfect vacuum is formed in the upper part of the tube. It is then fastened in the glass jacket by means of a cork near the lower end, and the weighed substance with the vessel is introduced into the barometer tube. The quantity of substance is so chosen that when vaporized it fills the tube almost to the stopper at the lower end of the jacket. This quantity is easily calculated from the formulas which follow. The tube, owing to the danger of breaking by the sudden vaporization of the substance, should be slightly inclined when the substance is introduced. The stopper must always be placed loosely in the small glass flask. After introducing the substance, which immediately vaporizes either wholly or in part, the vapor jacket is fastened in position and connected with the vessels attached to a and b. In the former is a liquid, the boiling point of which is at least 10° above that of the substance in the tube A. Water or anilin (B. P. 183°) is usually employed. The vapor of the hot liquid must be conducted in carefully at first. When the temperature has become constant the height h of the mercury in the barometer tube above the surface of the mercury in the trough is carefully determined by the method already described. The length h_1 of the barometer tube from about the middle of the lower cork to the surface of the mercury in the trough is also determined.

FIG. 15.

Calculation.—The vapor density d is calculated from the general equation:

$$d = \frac{g}{0.001293\, v_0} = \frac{g\, 76\,(1 + 0.00367\, t)}{v p\, 0.001293};$$

g is the weight of the substance in grams, v_0 the volume of the vapor at 0° and 76 cm. pressure, 0.001293 the weight in grams of 1 c.c. of air, and v the observed volume of the vapor in the barometer tube at the temperature t of the experiment and pressure p.

The pressure p is equal to the barometric pressure b reduced to 0° minus the column of mercury h reduced to 0°. As the temperature of the interior of the jacket and likewise the mercury within the jacket is t and that of the lower part of the mercury column t_1, the temperature of the room, we have:

$$p = \frac{b}{1 + 0.000181\, t_1} - \frac{h_1}{1 + 0.000181\, t_1} - \frac{h - h_1}{1 + 0.000181\, t} - f,$$

where f represents the vapor pressure of mercury at the temperature t, h_1 the height, and t_1 the temperature of the column of mercury from the middle of the stopper to the surface of mercury in the trough, and $h - h_1$ the height of the column of mercury in the vapor jacket at the temperature t. The above formula then can be written:

$$p = (b - h_1)\,(1 - 0.000181\, t_1) - (h - h_1)\,(1 - 0.000181\, t) - f\,*$$

For exact measurements the expansion of the barometer tube when heated must be taken into account. As the tube is calibrated for 15°, its volume v_t at $t°$ is.

$$v_t = v_{15}\,(1 + 0.000025\,(t - 15)).$$

v_t should therefore be substituted for v in the above expression for finding d.

An appreciable error is also introduced by the fact that the mercury column consists of two parts, which are heated to different and not accurately measured temperatures. For exact determinations, therefore, the recent modification of the apparatus (Fig. 16) is doubtless to be preferred. As the entire column of mercury in this case is heated to the temperature t, the expression for p is much simplified.

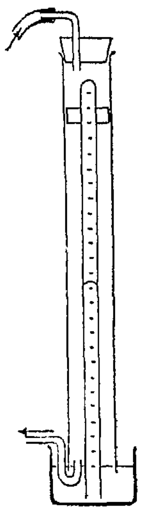

FIG. 16.

Application of the Methods of Dumas and Hofmann.—The advantage of the Gay-Lussac-Hofmann method over that of Dumas consists prin-

* For the reduction of the mercury column to 0°, see Landolt-Börnstein, Tables, p. 26, 1883; pressure of mercury vapor, *ibid.* p. 58.

cipally in that the substance is vaporized in a vacuum and, therefore, at a lower temperature than if vaporized at the atmospheric pressure. The method is preferable, therefore, for all compounds which at a higher temperature and pressure have a tendency to decompose or dissociate, and also in cases where only a small quantity of material is to be had. On the other hand, the application of the method is restricted to temperatures not much exceeding 200°, for the reason that mercury must be used in the experiment.

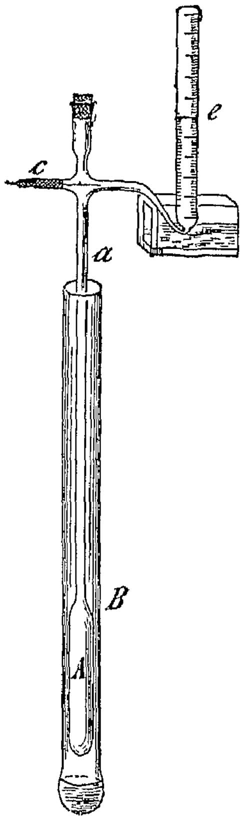

FIG. 17.

(*c*) METHOD OF V. MEYER (AIR DISPLACEMENT).

Principle.—A definite quantity of substance is introduced into an air chamber which is kept at constant temperature and provided with an arrangement by which water may be displaced by the air. If the temperature of the air is higher than the boiling point of the substance, the latter vaporizes and displaces a volume of air equal to the volume of the vapor formed. From this volume and the quantity of substance used, the vapor density may be easily calculated (see below).

Apparatus.—A cylindrical glass vessel *A* (Fig. 17) is provided at the top with a longer tube *a*. This vessel is placed in an outer glass jacket *B*, in which some suitable substance is heated to boiling, in order to maintain a constant temperature for the vessel *A*. For substances with high boiling points (sulphur, diphenyl, etc.) it is better to use a copper jacket instead of the glass.

The tube *a* is closed with a rubber stopper, and is connected with a calibrated tube *e* filled with recently boiled water. The air displaced by the vaporization of the substance is collected in this tube and its volume measured.

Solid or liquid substances are weighed in small flasks (Fig. 15) with or without corks. Volatile compounds are handled in thin-walled glass bulbs, each supplied with a small tube.

The introduction of the small flask into the vapor chamber can be accomplished in various ways. In figure 17 is represented the side tube *c* arrangement, which is usually employed. The small flask containing the substance is placed upon a glass rod which is introduced into the side tube, and the entrance to the vapor chamber finally closed by means of an elastic rubber tube which allows the glass rod to pass in and out When the desired temperature is obtained the small vessel is dropped from the glass rod into the heated vapor chamber, the bottom of which is covered with glass-wool or asbestos.

Method of Operation.—The vapor chamber is dried with alcohol and ether, and the apparatus then set up.

The glass or copper jacket contains a sufficient quantity of the heating substance, the boiling or melting point of which must be at least 30–40° higher than the boiling point of the substance in the vapor chamber. (Heating substances: Water, 100°; anilin, 183°; nitrobenzene, 211°; diphenylamine, 300°; paraffin-bath, 350°; sulphur, 448°.)

The jacket is then carefully heated; as soon as air-bubbles cease rising in the liquid which serves as the outlet to the vapor chamber, the small flask is introduced and supported by means of the contrivance at *c*. When the temperature of the vapor chamber becomes constant and the graduated tube *e* filled with water remains free from air for a considerable time, the substance is introduced in the manner already described.

The vaporization which follows immediately is shown by the rising of air-bubbles in the tube *e*. Each molecule of displaced air corresponds to one molecule of the substance vaporized.

From the volume of air contained in *e* the volume of the vapor at 0° and 76 cm. is then determined.

When air no longer escapes from the vapor chamber into *e*, the connection between the two is broken.

The volume of displaced air should be at least 30–40 c.c. The quantity of substance to be used, therefore, must be estimated. Ordinarily from 0.1 to 0.2 gm. are sufficient. Knowing the dimen-

sions of the apparatus and the temperature required, the quantity of substance can be easily calculated from the formula below.

The vapor chamber may be filled with hydrogen, nitrogen or carbon dioxide instead of air.

Calculation.—Let the weight in grams of the substance used in the experiment be represented by g, the volume in cubic centimeters of displaced air by v, the height of the water column in e by h, the temperature of the water = temperature of the room by t, and the barometric pressure by b; then the vapor density d is given by the expression:

$$d = \frac{g}{v_0\, 0.001293} = \frac{g\, 76\,(1 + 0.00367\, t)}{v p\, 0.001293};$$

p is the pressure, in centimeters of mercury, at which v is measured. This pressure is found from the expression:

$$p = \left(b - \frac{h}{13.596}\right)(1 - 0.000181\, t) - f,$$

where f is the vapor pressure * of water at the temperature t.

Application of the Method.—The method just described is characterized by its extreme simplicity.

In contrast with the Hofmann method, this procedure is applicable to higher temperatures. On the other hand, the Hofmann method is preferable for accurate determinations, and also for compounds which are easily dissociated or decomposed. For dissociable compounds the method of V. Meyer must be carried out with great care and sometimes rejected entirely. In other cases varying values are obtained for the vapor density, depending upon the size and form of the vapor chamber and the quantity of substance used.†

On the application of higher temperatures, see, among others, V. Meyer and Langer, Pyrochemische Untersuchungen, Vieweg, 1885; Mensching and V. Meyer, Zeit. phys. Chem. 1, p. 145, 1887; Nilson and Petterson, *ibid.* 1, p. 34; 2, p. 657, 1888, and 4, p. 208, 1889, and Jour. pr. Chem. (2), p. 33, 1886; Grünwald and V. Meyer, Ber. d. d chem. Ges. 21, p. 687, 1888; Biltz and V. Meyer, Zeit. phys. Chem. 4, p. 249, 1889.

Method of metal-displacement (Wood's metal): V. Meyer, Ber. d. d. chem. Ges 11, p. 2253, 1878, and Kohlrausch, Prakt. Phys VII, p 59, 1892.

* Landolt-Bornstein's Tables, p. 40, 1883

† Biltz, Zeit. phys. Chem. 2, p. 944, 1888.

(*d*) METHOD OF LUNGE AND NEUBERG.*

(*Victor Meyer's Procedure under Reduced Pressure.*)

Principle.—The air displaced by vaporizing a weighed quantity of substance is collected over mercury instead of water in the tube *C*, which can be brought into connection with the vapor chamber *A* or with the outer air by means of the cup *a*. The tubes *C* and *D*, connected by means of a flexible tube, form a mercury pump by means of which any pressure can be produced in the chamber *A*.

Apparatus (Fig. 18).—The arrangement of the vapor chamber *A*, as well as the contrivance at *c* and the outer jacket *B*, is the same as that described on page 38.

The apparatus is of larger dimensions than the simple apparatus of V. Meyer. The delivery tube *d* is at least 30 cm. long, and is connected with the tube *e* by means of a rubber tube, so that it can be brought into connection with the mercury pump *C b D* by means of the stop-cock *h*. The stop-cock, which is a Geissler obliquely-bored stop cock, can, by properly turning, be made to connect *e* with *C* or *a* with *C*, or can be entirely closed from *C* to *e* as well as to *a*.

The calibrated tube *C* (zero point at the top) is connected with *D* by means of the flexible tube *b*.

The flexible tube must be thick-walled and interwoven or wrapped with canvas. The rubber connections at *e* and *c* must be carefully chosen and frequently renewed. They should be wrapped with wire, and the stop-cock *h* should always be greased.

The reading of the top of the mercury in *C* and *D* is accomplished, for accurate measurements, by means of a cathetometer or by means of the Hofmann contrivance (p. 35).

Ordinarily the arrangement shown in figure 18 is sufficient.

A wooden millimeter-scale is fastened in a vertical position on *C* by means of the ring *r* which is placed in such a position that the upper edge, which is the zero point of the scale, is in the same horizontal plane as the top of the mercury.

A pointer *z* is fastened to the scale and is adjusted so that the

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* Lunge and Neuberg, Ber. d. d. chem. Ges. 24, p. 729, 1891.

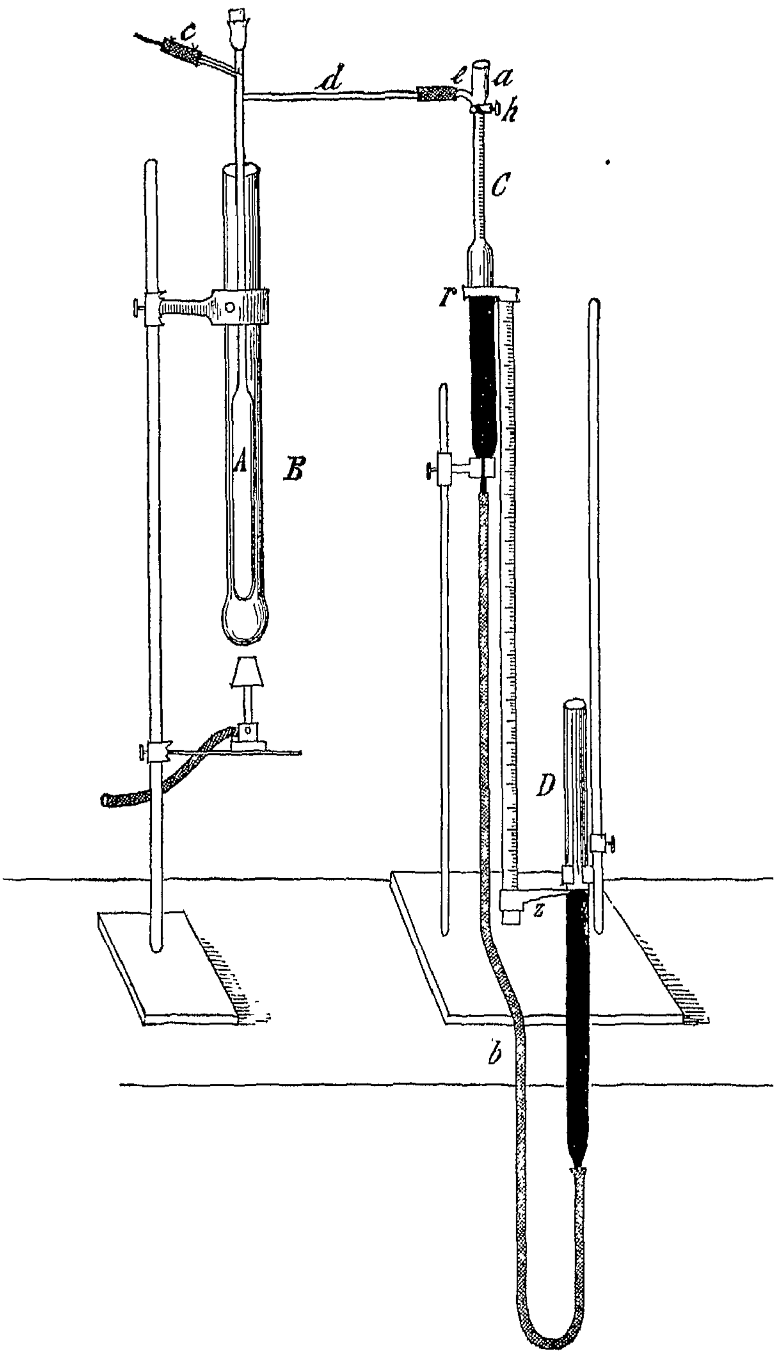

FIG. 18.

upper edge is in the same horizontal plane as the top of the mercury in *D*. The position of the upper edge of the pointer is then read on the scale.

Method of Operation.—The two parts of the apparatus, after drying with alcohol and ether, are firmly fastened to a stand and connected air-tight by means of a rubber tube.

The stop-cock *h* is then turned so that *C* is connected with *a*. The tube *D* is filled with recently boiled mercury and raised to such a height that the mercury flows into *a*. *h* is then closed and *D* lowered until a Torricellian vacuum is formed in *C*; the difference in height then of the upper surfaces of the two columns of mercury represents the ordinary barometric pressure. When filling the apparatus, air-bubbles cling for some time to the sides of the glass tube, and especially to the walls of the rubber tube, so that *D* must be frequently raised and lowered. It is better, therefore, after once filling, to allow the mercury to remain in the apparatus. For accurate determinations it is preferable to use a special barometer.

Suppose the barometric pressure to be 750 mm., and that the vapor density determination is to be made at 50 mm. The air in the apparatus is exhausted so far that, by connecting *A* with *C*, the perpendicular distance between the tops of the mercury columns in *C* and *D* is $750 - 50 = 700$ mm. The pointer *z* on the contrivance for reading off the pressure is fastened on 700 mm. *C* is then connected with *A* and the air which passes from *A* into *C* is removed, in that the connection *C*—*A* is closed and the connection *C*—*a* opened; by raising *D* until the mercury enters *a*, the air is completely removed. *h* is then closed so that *C* is neither in connection with *A* nor *a*, *D* is lowered and *C* is again connected with *A*; C—*A* is then closed and *C*—*a* opened and the air in *C* removed by raising *D*. By repeating this operation four or five times the desired exhaustion of the apparatus is practically attained. *A* is then connected with *C* and the upper edge of the ring *r* is placed at the top of the mercury column in *C*. At the same time *D* is fastened in the stand so that the top of the mercury column in *D* coincides with the upper edge of the pointer *z*, placed at 700 mm. If the pressure of 50 mm. in the

apparatus remains constant for five minutes, the stop-cock and rubber connections are tightly closed.

If the pressure remains constant, the connection $C - A$ is closed and $C - a$ opened, then by raising D the air in C is completely removed. If, then, after the vaporization of the substance in the chamber A, the pressure again becomes 50 mm., it is evident that for each molecule of substance vaporized one molecule of air passes from A into C. From the volume of air in C at 50 mm. pressure, the volume and vapor density of the vaporized substance is calculated by known methods.

The heating of A (p. 39) can be carried on during the exhaustion of the apparatus. To protect C from the heat, a card-board or asbestos screen is placed between A and C.

If a constant temperature has been attained and C has been exhausted to 50 mm. pressure in the above manner, A is connected with C and the experiment is begun.

The mercury in C falls immediately; as soon as the top of the column becomes stationary, the pressure in the apparatus is brought to exactly 50 mm. by raising and lowering D. The connection between C and D is then closed, the rubber stopper is taken out and the flame removed.

Calculation.—Let g represent the weight of the substance in grams, v the volume in cubic centimeters of displaced air contained in C, p the pressure, in centimeters of mercury, of the air in C at the time of reading the volume v, and t the temperature of the mercury (equals temperature of the room), then the vapor density is:

$$d = \frac{g\, 76\, (1 + 0.003367\, t)}{v p\ 0.001293}.$$

If h is the perpendicular distance between the tops of the columns of mercury in C and D at the time of reading v, b the barometric pressure, and f the vapor pressure of mercury at $t°$, then,—

$$p = (b - h)\ (1 - 0.000181\ t) - f. *$$

Application of the Method.—While the air-displacement procedure, in the simple form of V. Meyer, is not applicable for compounds which dissociate under the atmospheric pressure, the

* See Landolt-Börnstein's Tables, pp. 26 and 58, 1883.

working under reduced pressure has the advantage mentioned before for the Hofmann apparatus. Besides the greater simplicity in the method of operation, this method possesses another advantage over that of Hofmann in that the mercury is not heated. Naphthalene (B. P. 218°) can be investigated in the vapor of xylene (B. P. 140°), and mercury (B. P. 359°) in the vapor of diphenyl (B. P. 254°).

III. CAPILLARITY.

I. FROM THE RISE IN A CAPILLARY TUBE (The Capillarimeter).

Calculation.—The constant of capillarity, γ ($= a$), may be defined as the weight of liquid suspended per linear unit of contact between a liquid and a solid wall (mg. mm.).

Its value is given by the expression:

$$\gamma \cos \vartheta = \frac{r h s}{2}. *$$

ϑ represents the angle formed by the uppermost particle of liquid and the walls of the tube; r is the radius of the tube, and h the capillary rise, both measured in millimeters; and s is the specific gravity of the liquid.

Cos ϑ can not (as the earlier theory admitted) be placed equal to 1 in all cases; one must be content, therefore, in establishing the constant $\gamma \cos \vartheta$.

The constant is frequently calculated from $a^2 \cos \vartheta = r h$, where a^2 is the specific cohesion.

For aqueous solutions, the lowering of the capillarity of the solvent is usually considered; it is:

$$\gamma_w \cos \vartheta_w - \gamma_l \cos \vartheta_l = \tfrac{1}{2} r (h_w s_w - h_l s_l).$$

The corresponding constants for water and the solution are repre-

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* Ostwald, Lehrb. Allgem. Chem., 2. Aufl., Bd. 1, p. 514, 1891.

sented by the indices w and l. (J. Traube, Lieb. Ann. 265, p. 28, 1891.)

Apparatus.—The capillarimeter (Fig. 19) consists of a capillary tube 15 to 20 cm. long, and a scale made of porcelain or metal. The tube and scale are fastened together by means of small screws, so that the tube extends from 2 to 3 cm. beyond each end of the scale.

The scale, from 1 to 2 cm. wide, is graduated to 0.5 mm.; it terminates below in two points which coincide with the zero point of the scale. The position of these points must be adjusted with considerable care.

The stand A carries the clamp a; by means of the fine screw b, the clamp, and likewise the capillarimeter fastened in it, can be raised or lowered.

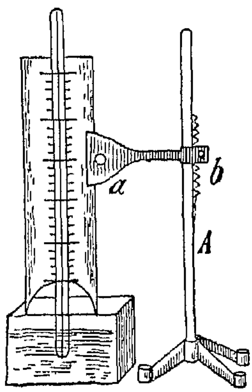

FIG. 19.

The capillary tube should have a radius of from 0.15 to 0.2 mm. The walls of the tube should be as thin as possible and, above all, the diameter of the tube should be uniform throughout. This is especially necessary inasmuch as the calculation of the capillary constant is made from the diameter of the tube at the place where the meniscus is situated. The uniformity of the bore of the tube is tested by passing a thread of mercury into the clean, well-dried tube of greater length. For this purpose the tube is fastened to a scale;* errors due to parallax in reading the scale should be avoided. If the tube is not sufficiently uniform, another is chosen or a correction table is calculated.

The mean radius is best determined by means of pure mercury.

The clean, dry tube, after being fastened to the scale, is repeatedly filled as full as possible with mercury, and the total length of mercury threads is measured (avoiding errors due to

* Since the work of Lothar Meyer, Berberich has introduced a mirror-scale which enables the observer to easily eliminate the error of parallax.

parallax). If the total length $= l$ mm., the total weight $= p$ mg., and the temperature of the mercury is t, then the radius of the tube is:

$$r = \sqrt{\frac{p(1 + 0.000181\,t)}{13.596\,\pi\,l}}$$

in millimeters. The variation in several measurements should not amount to more than one unit in the fifth decimal place.

The tube should always be kept perfectly clean.

At the end of the investigation the tube should be closed with black rubber; from time to time it should be cleaned with concentrated nitric acid. After each observation the tube should be cleaned and dried by sucking into it water and alcohol (not ether); this is accomplished by connecting one end of the tube with a sulphuric acid bottle and the other with the mouth or a pump. Saliva or rubber should never be allowed to enter the tube.

If the necessary precautions are always observed, the same tube can be used for several years.

An unclean tube is usually the cause of an imperfect wetting of the walls by the liquid, and of the irregular, jerky movements of the liquids. In such cases the cleaning can frequently be accomplished with nitric acid.

Method of Measurement.—The scale is placed in the support so that the tube stands as vertical as possible. The error introduced by a slight inclination of the tube is inappreciable. The vertical position is determined simply with the eye or by means of a plumb-line.

The liquid is placed under the tube in a small glass vessel. The dry points of the scale should touch the surface of the liquid simultaneously. The inclination, however, amounts to less than 0.1 mm. if the two points are not immersed simultaneously in the liquid; it is then desirable to always bring the same point to the liquid first.

When the points are adjusted, the liquid is slowly sucked up into the tube. The operation should be conducted so as to produce a perfect wetting of the tube.

The liquid is sucked (carefully avoiding the entrance of saliva into the tube) three times from 3 to 4 cm. above the final position

of the liquid meniscus, and is allowed to fall from 5 to 8 cm. When the liquid has been sucked up three times, it is allowed to fall in the tube, and the height assumed by the lower edge of the meniscus after one-half to one minute is read off (care being taken to avoid any error due to parallax). A microscope may be advantageously employed; or a cathetometer may be used in making the reading. Heating of the tube should always be prevented.

Ordinarily, the position of the liquid remains constant during one or several minutes, and then a gradual sinking begins, owing to a lack of perfect wetting of the tube; or a rising for volatile liquids. For exact measurements, a small correction must be applied to the observed height of the meniscus; the observed value should be increased by $\frac{1}{3}r$. The true value then is $h_{\text{corrected}} = h + \frac{1}{3}r$.

Care should be taken in all observations that small air-bubbles do not occur in the liquid in the tube, and that the column of liquid should at no place be separated. Especially for the more viscous liquids or with very narrow tubes it is important, after the capillary rise has been determined according to the above method, —by sucking the liquid up and allowing it to fall,—to confirm the result by sucking the liquid up once, forcing it down, and allowing it to rise of its own accord. The height attained by this capillary rise should not be more than $\frac{1}{10}$ of a mm. lower than the height attained by the first method.

The liquid and the tube should be warmed to the same temperature as that of the room before the experiment; it is also very important, in most cases, that liquids should be sucked up only from the surface; a change of concentration influences the result.

The observations are always made at a definite temperature, usually at 15 or 20°; the temperature coefficient for most liquids and for tubes of from 0.15 to 0.2 mm. radius amounts usually to only 0.1 to 0.2 mm. for 1° Celsius.

The observations should be repeated after cleaning and drying the tube with alcohol. The variations should not, at most, amount to more than 0.2 to 0.3 mm. About twenty observations may be made in an hour.

The constant $a^2 \cos \vartheta = r\,h$ is, for water at 15°:

= 15.09 (according to Volkmann),
= 14.70 (" Quincke),
= 14.88 (" Brunner),
= 15.12 (" Hagen),
= 15.24 (" Wolff),
= 14.77 (" Traube).

Weinberg, Zeit. phys. Chem. 10, p. 34, 1892; *ibid.* p. 38, literature.

2. THE DROP METHOD (The Stalagmometer).

Principle and Calculation.—If different liquids under definite pressures are allowed to drop from a horizontal, smooth surface of from 6 to 8 mm. in diameter, the weights of the drops are proportional to the weights of the liquids in the capillary tubes. If, therefore, definite volumes of different liquids drop from the same surface, the number of drops in the volume v are inversely proportional to the rise of the liquids in capillary tubes.

If z_w and z_r represent the number of drops contained in the volume v of water and some other liquid dropping from the surface a (Fig. 20), and $a_w^2 \cos \vartheta_w$ and $a_r^2 \cos \vartheta_r$ represent the corresponding capillary constant (p. 39), we have from the above proportion the equation:

$$a_r^2 \cos \vartheta_r = a_w^2 \frac{\cos \vartheta_w \cdot z_w}{z_r} = 14.90 \frac{z_w}{z_r},$$

and

$$\gamma_r \cos \vartheta_r = 7.45 \frac{z_w\, s_w}{z_r\, s_r},$$

where s_w and s_r represent the specific gravities of the water and the liquid.

Apparatus.—The apparatus consists of an outflow arrangement A as well as the pressure apparatus B, and is identical in its essential parts with Poiseuille's apparatus for determining the constant of viscosity; hence the constants of capillarity and viscosity may easily be determined together.

The stalagmometer A consists of a tube bent twice into a knee shape, the upper end of which expands into a globe in which a

definite volume v, of 6 to 8 c.c. capacity, is divided off by the two boundary lines b and c. The middle and lower limb of the tube is a capillary tube, the outer diameter of which is from 6 to 8 mm., while the inner diameter is chosen according to the height of the pressure column and length of the tube, so that the time of forming

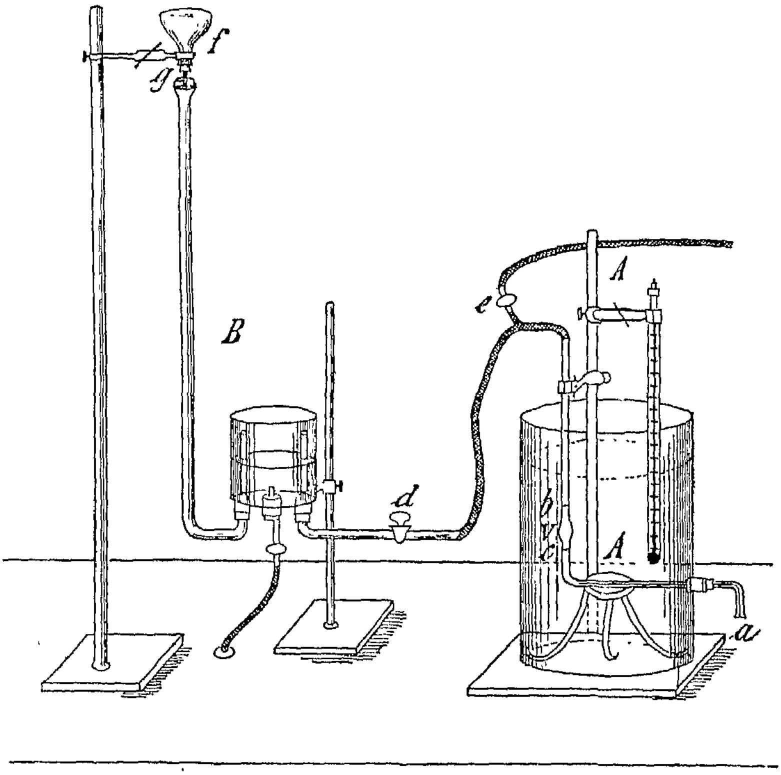

FIG. 20.

a drop will be at least four to five seconds. The drop-surface a (6 to 8 mm. in diameter) should be well polished, and the outer edge made as conical as possible (see Fig. 20) to prevent any drawing away of the liquid by the sides of the tube, so that only the under surface where the drop is formed will become thoroughly wet. The flow of liquid to the drop-surface must take place through a

capillary tube, otherwise an irregular whirling motion will be produced in the drop.

The conical grinding of the sides of the tube at the surface is unnecessary; by carefully greasing the outer walls of the tube near the surface the drawing away of the liquid can be prevented.

By means of the pressure apparatus the liquid can be made to flow out under constant or any desired pressure.

A wide glass tube about one meter high is connected with a Wulf bottle, in which the air is compressed, corresponding to the height of the pressure column. The filling with water takes place through the stop-cock *d*. The level of the water in the pressure tube is kept constant by means of the water in the vessel *f*, which gradually flows in, owing to the tilting of the piece of ground-glass at *g* when the surface of the water in the pressure tube is lowered. The stop-cock *e* is connected with an air-pump, which makes it possible to suck the liquid through *a* into the apparatus. The glass parts should be connected by means of black or red rubber tubing.

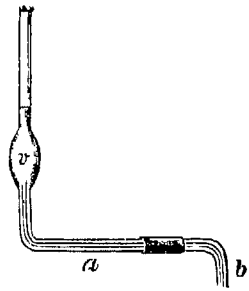

FIG. 21

If the apparatus is also to be used for determining the constant of viscosity (p. 53), it is better to divide *A* into two portions, connected by means of rubber (as in Fig. 21). *b* is a capillary knee-tube which must be removed in the determination of the constant of viscosity, in case its inner radius is not considerably greater than that of *a*. The knee-tube *a* (volume *v*, length and radius of the capillary tube) is then carefully measured by means of mercury and placed in a cylindrical glass water-bath. For determining the capillary constant alone, the water-bath (Fig. 20) is not necessary. For the simultaneous determination of constants of capillarity and viscosity, see J. Traube, Ber. d. d. chem. Ges. 19, p. 871, 1886.

Method of Operation.—The liquid at the temperature of the room and as free as possible from dust is sucked up into the apparatus by connecting the stop-cock *e* with the pump, until the level of the liquid reaches the mark *b*. The connection is then

made with the pressure apparatus and the number of drops contained in the volume *v* counted.

If the outflow is sufficiently slow, the operator with a little care and practice can determine the exact moment when the lower edge of the meniscus passes the marks *b* and *c*, and estimate the corresponding quantity of liquid with certainty to 0.1 to 0.2 of a drop. If the observation of the moment when the liquid passes the mark *b* is not made sharp enough, connection is again made with the air-pump, until finally for the mark *b* a whole drop separates.

This method leads to accurate results; repeated observations should not show variations of more than 0.2 or 0.3 in the number of drops contained in the volume *v*. The drop-surface and capillary tube should be absolutely clean. A variation in the speed of the outflow, due to the presence of dust in the capillary tube, gives rise to appreciable errors; the rate of outflow, therefore, is always fixed as nearly constant as possible. The larger air-bubbles in the drop should be avoided.

For the majority of liquids, whose constants of viscosity and rates of outflow do not differ more than fifty per cent. from the corresponding values for water, the pressure, under which the liquids flow out slowly (one drop in five seconds), can be kept constant. If, however, very viscous liquids are to be compared with easily flowing liquids (aqueous glycerin, cane-sugar solution with water), the pressure columns are to be shortened or lengthened so that the speeds of outflow are not very different.

The error introduced by using equal pressures in such cases seldom amounts to more than one to two per cent. The difference between the capillary constants γ calculated by the capillary-rise method and the drop method amounts to less than one per cent.

The determination of the capillary constant at higher temperatures is best accomplished by the drop method; at the boiling point by the capillary-rise method: R. Schiff, Lieb. Ann. 223, p. 47, and Gazz. chim. Ital. 14, p. 1, 1884. Determination at the melting point: J. Traube, Ber. d. d. chem. Ges. 24, p. 3074, 1891.

Application of Capillary Constants.—The constant of capillarity has hitherto been of little use for chemical purposes.

On the relation to the constitution of homogeneous organic liquids, see the work of Schiff, already cited. The constant of

capillarity is of still greater use in the domain of (aqueous) solutions.

1. The constant for water is often considerably lowered by dissolving organic compounds in it. The constant is closely related to the constitution of the dissolved substance; for isomeric compounds it is frequently very different. The constant is of considerable value, therefore, in determining the constitution of compounds. J. Traube, Lieb. Ann. 265, p 28, 1891.

2. The capillarity constant is of importance from an analytical standpoint.

Many compounds (especially electrolytes) in concentrated solution influence the constant of water very little, while other substances in dilute solutions often lower the constant considerably.

The capillarity constant makes it possible, therefore, to determine, often very accurately, the concentration of a solution, and hence may be used in the approximate quantitative determination of many substances present in small quantities in a solution which may at the same time contain large quantities of other substances (mineral acids and bases as well as salts). The constant is also of value in determining the degree of purity of a dissolved substance.

Duclaux, Ann. chim. Phys (5) 13, p. 76, 1878; J. Traube, Jour. prakt. Chem., N. F. 31, p. 177, 1885. Application to the determination of the basicity of acids, J. Traube, Ber. d d. chem. Ges. 24, p 3074, 1891.

IV. THE CONSTANT OF VISCOSITY.

I. METHOD OF POISEUILLE-OSTWALD.

Principle and Calculation.—The constant η of viscosity may be defined as the work required to move, in unit time, two layers of liquid of unit surface in parallel and opposite directions; the distance moved being equal to the distance between the two layers of liquid.

The constant is determined by different modifications of the outflow method of Poiseuille. The time required for a definite volume

of liquid under a definite pressure to flow through a capillary tube is determined, and the constant of viscosity calculated according to the formula of Finkener: *

$$\eta = \frac{r^4 \pi h s}{8 l v} t - \frac{v s}{8 \pi g l} \frac{1}{t},$$

where η is the constant of viscosity of the liquid;
s the specific gravity of the liquid;
r and l the radius and length of the capillary tube (in cm.);
v the volume of liquid flowing out in the time t (cm. sec.);
h the height of the pressure column in centimeters, under which the liquid flows out;
g the acceleration due to gravity = about 981.2 and π the known constant value.

As all the values except s and t are constant for the same apparatus, the above formula may be written:

$$\eta = c s t - \frac{c_1 s}{t}.$$

The constants c and c_1 are to be determined for each apparatus. The dimensions of the apparatus are so chosen that the value of $c_1 \frac{s}{t}$ is only a small per cent. of the value η. Instead of η, it is frequently sufficient to determine the "specific viscosity" z of the liquid. By this is meant the time of outflow of the liquid (multiplied by 100) at any temperature, divided by the time of outflow for water at 0°. We have, therefore,

$$z = \frac{100\, t}{t_w}.$$

The determination of the constants of the apparatus is not necessary in this case.

Apparatus (Fig. 22).—A vertical capillary tube b is fused at the ends to the two wider tubes e and d, so that the change from the capillary to the wider tubes is as sharp as possible. A bulb k is blown in the upper tube d, in which a definite volume v of liquid can be measured off by means of the two marks a and c.

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* Gartenmeister, Zeit. phys. Chem. 6, p. 525, 1890; also Wilberforce, Phil. Mag. (5) 31, p. 407, 1891.

This simple apparatus is fastened by means of a rubber stopper in a large glass bell-jar of 15 to 20 liters capacity, which is filled with water and arranged so that the temperature may be determined accurately to 0.1°.

The pressure under which the liquid flows out in this apparatus is found by multiplying the specific gravity of the liquid by the varying height of the pressure column during the investigation.

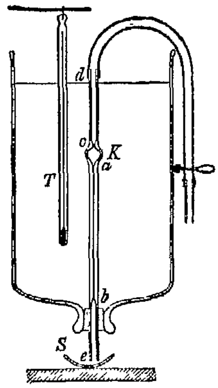

FIG. 22.

The mean height of the pressure column may be placed equal to the height h of the lower mark a above the lower opening of the capillary $= h_{,}$, increased by half the distance from a to $c = h_{,,}$, therefore $h = h_{,} + h_{,,}$.

For exact measurements it is desirable to use two or three different outflow tubes.

The volume of the bulb and the dimensions of the capillary tube are accurately measured by means of mercury,—best before the apparatus is set up. For the measurement of capillary tubes, see page 46.

The dimensions of the separate parts of the apparatus best adapted to this work lie between the following limits:

v = 4 to 8 c.c.
r = 0 025 to 0.030 cm.
l = 30 to 40 cm.
$h_{,,}$ = 1 to 2 cm.

The time occupied in the investigation is determined either with the help of an ordinary seconds watch or better, a chronograph; in the latter case the time is measured to the fraction of a second.

Method of Operation.—After carefully cleaning the capillary tube, the apparatus is filled with the clear liquid free from dust by means of a pump from below. By closing the black-rubber tube with a glass rod, the outflow of the liquid is prevented until the temperature of the liquid is the same as that of the water-bath. It is to be observed that the constant of viscosity, in most cases, varies to a high degree with the temperature.

When the experiment is to be commenced the glass rod is removed, and the time required for the passing of the meniscus from

the upper mark c to the lower mark b is measured by means of the chronograph. The liquid is not allowed to drop from the lower end of the tube, but the outlet end is immersed in a liquid contained in a small vessel.

The experiment is always repeated. Greater differences than 0.2 per cent. in the values of t are usually to be traced to the lodging of small solid particles at the top or in the capillary tube. The tube is therefore frequently examined with a microscope.

Before using, the apparatus is first tested by experimenting with water. The following table contains the constants of viscosity for water at different temperatures:

Temperature.	*Poiseuille* η	*Sprung* η	*Traube* η
0	0,018 142	0.018 136	0.01 824
10	13 351	13 271	1 333
20	10 296	10 214	1 032
30	08 212	08 186	0 819
40	06 718	06 725	0 669

Poiseuille's apparatus for the simultaneous determination of the constants of viscosity and capillarity, see p. 43, and Ber. d d. chem. Ges. 19, p. 872, 1886; a recent form of apparatus especially adapted to high temperatures, see Ostwald, Lehrb. allgem. Chem., 2. Aufl., Bd. 1, p. 550, 1891.

Relation of the constant of viscosity to the constitution of a liquid, see Gartenmeister, Zeit. phys. Chem. 6, p. 524, 1890, and Handl and Pribram, *ibid.* 9, p. 529, 1892. Constant of viscosity for solutions, Arrhenius, Zeit. phys. Chem. 1, p. 285, 1887; Reyher, *ibid.* 2, p. 744, 1888; Wagner, *ibid.* 5, p. 31, 1890; Lauenstein, *ibid.* 9, p. 417, 1892. Influence of temperature, Grätz, Wied. Ann. 31, p. 25, 1888; Stoel, Phys Revue 1, p. 513, 1892. Tables and earlier literature, Landolt-Börnstein's Tables, p. 153, 1883.

V. SOLUBILITY.

The solubility is referred either to a constant quantity of the solvent or, better, to a constant weight or constant volume of the solution. It may also be referred to the number of molecules.

The solubility of a solid compound is determined by shaking the solvent for at least two to three hours at constant temperature with an excess of the powdered substance.

The thermostat described by Ostwald (p. 65) may be used for this purpose. The flask filled with the solvent is placed in the thermostat; the Raabe turbine may be used to advantage as a stirring apparatus. When the solution in the thermostat has become perfectly clear, a definite portion is removed by sucking up into the small pipette (Fig. 23) proposed by Landolt. The pipette is closed by means of a glass cap. If the solubility is determined at higher temperatures, the pipette must be previously warmed. The quantity of solution is determined from two weighings of the pipette; for determining the quantity of dissolved substance, the contents of the pipette are washed into a suitable vessel.

FIG. 23.

The accuracy of the result is determined by conducting a parallel observation. The relation of the solubility and temperature is generally represented graphically.

See also the apparatus of Reicher and Van Deventer, Zeit. phys. Chem. 5, p. 560, 1890; for carrying out a large number of solubility determinations, see the apparatus of Noyes, Zeit. phys. Chem. 9, p. 606, 1892; see also Schröder, *ibid.* 11, p. 453 1893. Determination of solubility by means of the electric conductivity, see F. Kohlrausch and Rose, Ber. Berl Akad. 26, p. 453, 1893.

Solubility tables: Landolt-Börnstein's Tables, p. 154 1883.

Solubility of salts, see, among others, Engel, Ann. chim. Phys. (6) 17, p. 338, 1889; Meyerhoffer, Zeit. phys. Chem. 5, p. 97, 1890; Bodländer, *ibid.* 7, pp. 315 and 358, 1891; Tresor, *ibid.* 7, p. 469, and Lobry de Bruyn, *ibid.* 10, p. 782, 1892.

Solubility of organic compounds: Carnelley and Thomson, Jour. Chem. Soc., p. 782, 1888.

Apparatus for determining the absorption of gases: Timofejew, Zeit. phys. Chem. 6, p. 141, 1 90; L. W. Winkler, Ber. d. d. chem. Ges. 24, p. 89, 1891; Bohr and Bock, Wied. Ann. 44, p. 318, 1891.

Osmotic pressure. Apparatus: Adie, Jour. Chem. Soc., p. 344, 1891; Tammann, Zeit. phys. Chem 9, p. 103, 1892, and Walden, *ibid.* 10, p. 699, 1892.

Diffusion. Apparatus: Scheffer, Zeit. phys. Chem. 2, p. 391, 1888; Chabry, Jour. der Phys (2) 7, p. 115, 1888; Stefan, Wiener Monatshefte, 10, p. 201, 1889; Wiedeburg, Wied. Ann. 41, p. 675; Arrhenius, Zeit. phys. Chem. 10, p 52, 1892, and Abegg, 11, p. 249, 1893; Pickering, Phil. Mag (5) 35, p. 127, 1892.

Reaction, velocity, and chemical equilibrium. Recent literature: Warder, Ber. d. d. chem. Ges. 14, p. 1361, 1881; Reicher, Lieb. Ann. 228, p. 257, 1885; Ostwald, Jour. prakt. Chem. (2) 35, p. 112, 1887; Landolt, Ber. d. d. chem.

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Ges. 19, p. 1343, 1886; Arrhenius, Zeit. phys. Chem. 1, p. 109, 1887, and 4, p. 226, 1889; Menschutkin, Zeit. phys. Chem. 1, p. 611, 1887; 5, p. 589, and 6, p. 41, 1890; Bull. Ac. Belg. (3) 31, p 559, 1891; Konowalow, Zeit phys. Chem. 1, p. 63, 1887, and 2, pp. 6 and 380, 1888; Ostwald, Zeit. phys Chem. 2, p. 127, 1888; Meyerhoffer, *ibid.* 2, p. 585; Spohr, *ibid.* 2, p. 194; Giersbach and Kessler, *ibid.* 2, p. 676; Will and Bredig, Ber. d d. chem. Ges. 21, p. 2777, 1888; Burchard, *ibid.* 2, p. 796; Bonz, *ibid.* 2, p. 865; Lengfeld, Amer. Chem. Jour. 11, p. 40, 1889; Hecht, Conrad, and Brückner, Zeit. phys. Chem. 3, p. 450, 1889; 4, p. 273, 1889; 5, p. 289, 1890, and 7, p. 274, 1891; Walker, *ibid.* 4, p. 319, 1889; Fulda, *ibid.* 6, p. 491, 1890; Montemartini, Rendic. Acc. Lincei 6, p. 263, 1890; Evans, Zeit. phys. Chem. 7, p. 337, 1891; Schükarew, *ibid.* 8, p. 76, 1891; Bugarsgky, *ibid.* 8, p. 398, 1891; Wildermann, *ibid.* 8, p. 661, 1891; 9, p. 13, 1892; Muller and Hausser, Compt. rend. 114, pp. 549 and 760, 1892; Henry, Zeit. phys. Chem. 10, p. 97, 1892; Uno Collan, *ibid.* 10, p. 130; Trevor, *ibid.* 10, p. 321, 1892; Hjelt, Ber. d. d chem. Ges. 24, p. 1236, 1891.

VI. THE ELECTRIC CONDUCTIVITY OF LIQUIDS.

1. METHOD OF F. KOHLRAUSCH.*

Apparatus and Method in General.—The method of Kohlrausch depends upon the use of alternating currents, in connection with the Wheatstone bridge.

The element E (Fig. 24) is connected with the induction coil J, the wires of which are fastened to the measuring bridge B by means of binding screws. The circuit of the bridge is made complete by means of a metallic wire which passes through each of the binding screws and finally to the resistance solution W and the comparison resistance R. To the binding screw between W and R is fastened a telephone wire, the other end of which leads to a movable metallic slide on the bridge.

By closing the circuit the element is set in operation, and the slide can be placed at such a position on the bridge that no cur-

* Kohlrausch, Wied. Ann. 6, pp. 1 and 145, 1879; 26, p. 161, 1885; and 49, p. 225, 1893; Ostwald, Zeit. phys. Chem. 2, p. 560, 1888.

rent will pass through that part of the conductor in which the telephone is introduced.

The interposed telephone furnishes a means of determining the proper adjustment, instead of the galvanometer or dynamometer, in that when the slide is at the proper position the telephone is either silent or produces a minimum tone which is augmented by moving the slide in either direction on the scale of the bridge.

From the position of the slide corresponding to the minimum tone, we deduce by means of Kirchhoff's laws * the proportion $W : R = a : b$.

W is the resistance of the liquid and the electrode vessel; R is the interposed comparison resistance; a and b represent the number of divisions on the scale of the bridge, to the left and right of the slide when properly adjusted. The unknown resistance of the liquid or the reciprocal value, the electric conductivity, may be calculated from the above proportion according to page 69.

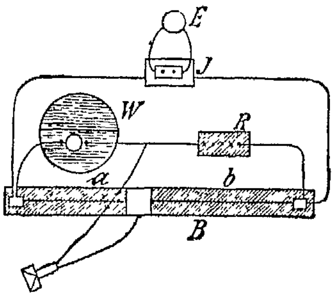

FIG. 24.

The Apparatus in Detail.

The Element.—A small Bunsen chromic acid element is sufficient. For the preparation of 1 l. of solution, 92 gm. of pulverized potassium bichromate (or a corresponding quantity of the more soluble sodium salt) and 94 c.c. of concentrated sulphuric acid are rubbed together to a uniform pasty liquid; 900 c.c. of water are then carefully added while stirring.

The Induction Apparatus.—According to Ostwald, the smallest induction coil used for medical purposes is best adapted to this work. The rapidity of the vibration of the interrupter is increased still further by filing the little block of iron on the spring down to rather small dimensions (1 or 2 mm.). The mini-

* Ostwald, Allgem. Chem. I, p. 537, 1885; and Kohlrausch, Prakt. Phys. VII, p. 255, 1895.

mum tone of the telephone is sharper if the sliding brass tube is removed from the apparatus.

The sharpness of the telephone depends largely on the nature of the induction apparatus used,* especially on the speed with which the current is alternated. If, therefore, the tone-minimum is not sharp, different induction coils should be tested, and the most suitable selected.

The Measuring Bridge.—Instead of the cylindrical bridge † proposed by Kohlrausch, the bridge which is ordinarily employed may be used. The simplest form ‡ of the same (Fig. 25) is constructed as follows:

A paper (or wooden) scale, graduated in millimeters, is fastened on to a dry board of 110–120 cm. in length and 4–6 cm. in breadth. A metallic wire is stretched along the scale by means of the screws a and a_1 on the ends of the board. Two brass plates are fastened by means of the screws b and b' on to the board, perpendicular to the scale, so that their inner edges pass exactly through the divisions 0 and 100 on the scale. The screws b and b' serve also for fastening the wires from the induction apparatus and the resistances.

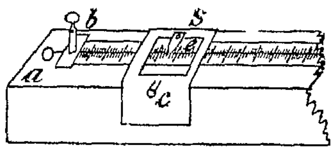

FIG. 25

The bridge wire, which is about 0.2 mm. in diameter, should be made of perfectly clean German silver, or of platinum containing iridium. The German silver wire, owing to its gradual oxidation in the chemical laboratory, gives rise to irregular sounds in the telephone; the wire should therefore be renewed from time to time.

For all exact measurements the uniformity of the wire should be tested and the wire calibrated before use. This may be done by the method of Strouhal and Barus (p. 73).

* Kohlrausch, Wied Ann. 6, p. 8, 1879.

† Kohlrausch, Wied Ann. 11, p. 653, 1880.

‡ A modified form, see Ostwald, Zeit. phys. Chem. 2, p. 562, 1888; Wiedemann and Ebert, Phys. Prakt. 1, p. 385, 1890.

The slide *s* of the measuring bridge, in its simpler form, consists of a rectangular, bent-down, metal frame with a small binding screw *c*, with which the telephone is connected. It is adjusted to the bridge so that it may be easily moved. In the middle of the frame and in contact with the bridge wire, is an elastic German silver needle, the flattened point of which is so constructed that it is always in perfect contact with the wire. The sensitiveness of the telephone depends on the kind of contact.*

The Telephone.—Care should be exercised in the choice of the telephone. The Bell telephone is well adapted to this work. Ostwald recommends the telephone of Ericsson, in Stockholm, as being very sensitive.

The sounds proceeding from the induction apparatus are annoying at first to the unpracticed. A small bulb or some wadding placed in the ear will remove this inconvenience. One learns very quickly, however, without this, to distinguish between the two sounds.

The Comparison Resistance.—Three resistances of 10, 100, and 1000 units (Ohm or Siemens) are sufficient. More appropriate, however, and far more convenient is the use of a complete resistance-box, the greatest resistance of which amounts to 2000 Siemens units. By using greater resistances, better results are obtained; it is better to work with different electrode distances. The best results are usually obtained with resistances of from 100 to 1000 units.

The resistances should be wound † bifilar, and should be compared, at least twice a year, with a standard resistance; at all events, one should satisfy himself by testing the apparatus, from time to time, with solutions of known resistances.

As the resistance varies with the temperature, it is necessary for accurate determinations to make the small temperature correction (see p. 70).

The Electrode Vessels.—Three different vessels are used for

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* Elsas, Wied. Ann. 44, p. 668, 1891.

† A new kind of winding by Chaperon, Elsas, Wied. Ann. 44, pp. 675 and 678, 1891; and F. Kohlrausch, *ibid.* 49, p. 233, 1893.

this purpose, according to the nature of the liquid to be investigated.*

1. For liquids of rather high conductivity (concentrated aqueous solutions of salts, mineral acids and bases).

For such solutions, use may be made of the vessels employed by Kohlrausch † (Fig. 26).

Two cylindrical beakers, which are reduced in size at the lower end, are joined together by means of a tube of about 9 mm. in diameter. The vessel contains from 12 to 25 c.c. of liquid. The electrodes consist of platinum, and are soldered to a copper wire which is introduced through a cover of hard rubber.

2. For liquids of moderate conductivity (dilute aqueous solu-

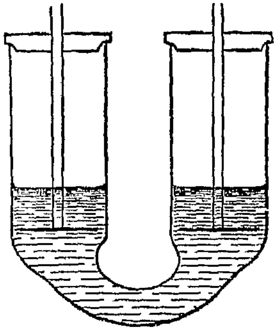

FIG. 26.

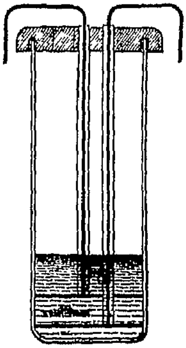

FIG. 27

tions of salts, mineral acids and bases, about $\frac{1}{32}$ to $\frac{1}{1024}$ normal; also concentrated solutions of many organic acids and bases).

The resistance vessel best adapted to such solutions is that proposed by Arrhenius (Fig. 27).

Two circular plates of heavy sheet-platinum from 3 to 4 cm. in diameter are soldered, by means of silver solder and borax, to heavy copper wires; the distance between the plates should be about 1.5 cm. The wires are enclosed in narrow glass tubes

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* [See also Kohlrausch, Wied. Ann. 51, p. 346, 1894, for special forms of electrodes and vessels.—TR.]

† Kohlrausch, Wied. Ann. 6, p. 6, 1879.

which are carefully filled with thick liquid asphaltum. The joint between the platinum and the glass should be well covered with the asphalt glue. The wires are introduced through a cover of hard rubber which is fastened by means of a groove on to the glass cylindrical vessel. It is advantageous to have two such vessels with the electrodes 1 and 2 cm. apart.

3. For liquids of low conductivity (most dilute solutions of organic acids and bases, especially aqueous solutions of neutral organic compounds, as well as homogeneous organic liquids and their mixtures).

For such liquids use is made of very narrow electrodes with greater surfaces; the apparatus of Pfeiffer* (Fig. 28) is well adapted to this work.

Two glass tubes R and R_1, of 3 and 3.6 cm. in their outer diameters, are covered to a length of 13 cm. with platinum foils P_1 and P, the smaller tube being covered on the outside and the larger tube on the inside.

The platinum-foil must form complete immovable cylinders; these cylinders are fastened to the outer glass surface by means of platinum wires. The larger platinum cylinder (soldered together by means of silver) is shoved into the wider tube. The smaller tube, after fusing together at the top, is then placed in the larger, so that the two platinum surfaces form concentric cylinders. On account of the large area, the surface of the platinum need not be covered with platinum-black (see p. 64).

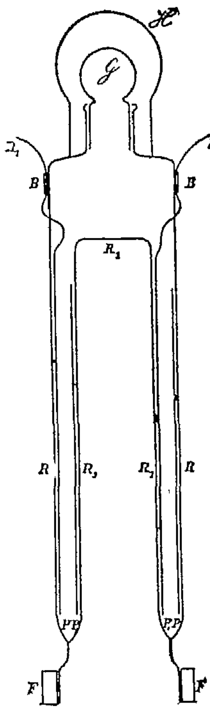

FIG. 28.

The two tubes are then melted together at the bottom, as shown in the figure; and at the opposite end the outer tube is drawn out into a narrow neck, in which can be placed a glass stopper G which, in turn, is covered by the glass covering H. D and D'

* Pfeiffer, Wied. Ann. 25, p. 233, 1885.

are the two electrodes leading to the platinum wires fused into B and B_1. The whole vessel (30 cm. high) is supported by means of the glass tubes fused in at the bottom, which are fastened to the strong brass foot F.

If a resistance vessel is to be used, it is best to restrict one's self to the form proposed by Arrhenius (Fig. 27) which, by the application of larger resistances, is sufficient for the majority of liquids.

The electrodes must always have a sufficiently large surface; a surface which is too small is accompanied by too great a current density, which frequently produces the phenomenon of polarization; the sharpness of the minimum tone depends largely on the frequency of the replatinizing of the surface.*

For this purpose the electrodes are immersed in a dilute solution of platinum chloride acidulated with hydrochloric acid, and the current of a single cell is conducted through, alternating frequently the direction of the current between the electrodes; or a small piece of zinc is brought in contact with the platinum surface until the plates are covered with a coating of black, spongy platinum.

According to Grotrian,† the well-platinized electrodes should be saturated with hydrogen by immersing them as kathode in dilute sulphuric acid. It is especially necessary that the electrodes be well platinized.

The Thermostat.—On account of the great influence of temperature on conductivity,‡ an accurate measurement of the temperature is very important.

Although Kohlrausch § has observed an influence of liquid baths on the minimum tone, and therefore made his determinations in air at the temperature of the room, yet the following, essen-

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* Kohlrausch, Pogg. Ann 148, p. 143, 1873, and *ibid.* 49, p. 235, 1893.

† Wershofen, Zeit. phys. Chem. 5, p. 486, 1890.

‡ For most electrolytes, a change of one degree Celsius changes the conductivity about two per cent.

§ Kohlrausch, Wied. Ann 26, pp. 172 and 184, 1885; Kohlrausch also observed that the telephone, if too near the apparatus, was influenced by the induction coil. See also Kohlrausch, Wied. Ann. 49, pp. 242 and 247, 1893.

tially the arrangement proposed by Ostwald (Fig. 30), is to be preferred for convenience.

The electrode vessel is supported in the iron water-bath *A* of 10 to 20 l. capacity, by means of a half-circular wooden cover.

A temperature regulator *B*, constructed in the ordinary manner, is fastened to this water-bath as shown in figure 30.

The regulator consists of a U-tube in which is fastened, by means of a rubber stopper, a cylindrical tube *C*. This tube (Fig. 30) is filled with oil or a concentrated solution of calcium chloride, and then connected with the U-tube (Fig. 29). A

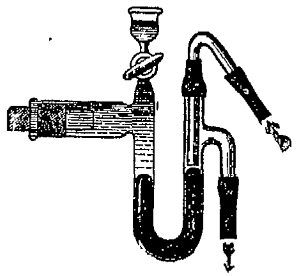

FIG. 29.

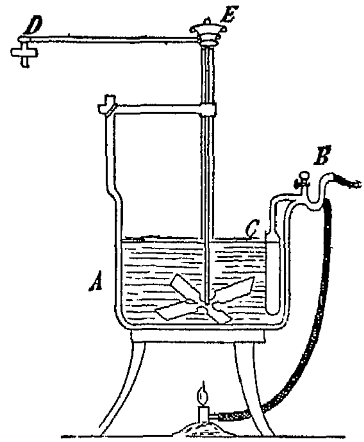

FIG. 30.

sufficient quantity of mercury is then conducted in through the funnel, after which, by suitably inclining the U-tube, the air in the part between the mercury and the funnel is completely replaced by oil or calcium chloride solution. The inflow and outflow of gas is indicated by the direction of the arrows.

To increase the sensibility, the inner portion of the gas-inlet tube is cut off at right angles. A very small side-opening in the same prevents the putting-out of the flame. By conducting in or removing liquid, by means of the funnel, the position of the top of the mercury column near the gas-inlet tube can be so regulated that widely varying temperatures may be obtained.

As a motor, the windmill of Ostwald * may be used. It is advantageous in this case to have the fans made of thin aluminium plates.

The use, however, of Raabe's turbine seems to me, in general, to be more appropriate. The everywhere purchaseable turbine *D*, after thoroughly oiling the parts of the apparatus, is connected by means of a cork to a double wheel *E*, which turns on a brass axis. From *E* the motion is transferred to a smaller wheel or, as in the figure, directly to the stirrer which consists of a glass rod fastened to *E* and provided at the lower end with a glass or wooden paddle; the glass rod rotates in a wider, well-oiled glass tube. By employing this thermostat, it is possible to maintain the temperature constant to 0.05°. For temperatures of 50° and over, the water is covered with a layer of paraffin; for temperatures above 80°, an altered thermostat is used as described by Bersch.†

The Contact.—The connection of the different parts of the apparatus is made by means of strong copper wires, which are as short as possible and fastened to suitable metallic clamps. A perfect contact is, above all, very important. The places of contact of the wires and the binding screws are carefully cleaned from time to time with a file and sand-paper; the binding screws should be well tightened, the stopper placed firmly in the rheostat, and the needle of the slide brought in good contact with the wire of the bridge. The contact with the electrode wires is made by means of small cups of mercury which, like the electrode vessel, are placed in the opening of the wooden cover of the thermostat. The copper wire of the electrodes should be carefully cleaned, moistened with hydrochloric acid and immersed in the mercury.

The Nature of Liquids to be Examined.

Water.—For establishing the conductivity, aqueous solutions are of prime importance; it is necessary, therefore, to exercise special care in the selection of the water to be employed. Water exhibits very different degrees of conductivity, depending upon

* Ostwald, Zeit. phys. Chem. 2, p. 565, 1888.

† Bersch, Zeit. phys. Chem. 8, p. 384, 1891.

the manner of distillation and preservation, while perfectly pure distilled water exhibits an extremely low conductivity.

The purest water obtained by Kohlrausch in a platinum apparatus had a conductivity of $k = 0.25 \times 10^{-10}$, compared with the mercury unit of $0° = 10^8$; however, it is sufficient, in general, to have water for which $k = 1.10^{-10}$ to 2.10^{-10}. For the meaning of k, see page 70.

The distillation of water, according to Kohlrausch, is carried on in a distillation apparatus with a tinned coiled tube.* Such water preserves (or diminishes) its conductivity if it is placed in a glass flask which has been used for a long time for distilled water.

In the investigations of liquids of high conductivity (concentrated salt solutions) the correction † for the conductivity of the water employed may be neglected; on the other hand, with dilute salt solutions and other aqueous liquids of low conductivity, the conductivity of the water must be first determined, just as that of a solution (see p. 69), and taken into account. For solutions of very low conductivity—*e. g.*, neutral organic compounds—the correction, which can be only imperfectly determined, is so great that, even with the greater sharpness of the minimum tone, an exact determination of the conductivity is not possible.

Solutions.—The substances employed must be pure, as the conductivity is often influenced by very slight traces of impurities.

The conductivity for acids, bases and salts is referred to the number of equivalents in one liter of solution; Ostwald denotes with $v = 32, 64 \ldots\ldots 1024$ those concentrations which contain $\frac{1}{32}, \frac{1}{64} \ldots\ldots \frac{1}{1024}$ equivalent weights in grams, in one liter of solution. For chemical purposes, solutions of $v = 32$ to $v = 1024$ are usually employed.

The introduction of the previously warmed solution into the electrode vessel is best accomplished after the solution has been

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* Kohlrausch, Wied. Ann. 26, p 170, 1885: Kohlrausch and G otrian, Pogg. Ann. 154, p. 3, 1875; Kohlrausch, Wied. Ann. 6, pp. 36 and 49, 1879, and 11, p. 653, 1880. Nernst, Zeit. phys. Chem. 8, p. 120, 1891, obtained water of $k = 2.10^{-10}$ by freezing ordinary distilled water; Van 't Hoff and Reicher, Zeit. phys Chem. 2, p. 778, 1888.

† Kohlrausch, Wied. Ann. 26, p. 191, 1885.

prepared ready for the experiment. However, the different dilutions can be obtained (of course, somewhat less accurately) in the resistance vessel. To accomplish this, half of the solution is removed by means of a suitable pipette, and an equal quantity of previously warmed water added. In this manner the dilution is increased two-, four-, eightfold, etc.

All solutions must be investigated in a fresh condition, for the conductivity of solutions of most organic compounds as well as many mineral salts, acids and bases, after twenty-four hours, shows, for unknown reasons, a variation.*

For dilute solutions of acids and bases (HCl, H_2SO_4, $C_2H_4O_2$, KOH, $NaOH$, NH_3), Kohlrausch † has shown that at the electrode there is a noticeable absorption of the substance, which apparently does not take place with neutral salts. This absorption produces, after a time, a perfect constancy in the minimum tone. If this phenomenon is of a general nature, and depends upon a real change in the concentration of the liquid, the inconvenience can, as suggested by Kohlrausch, be removed only by using larger resistance vessels of about 500 c.c. capacity.

Method of Operation.—As soon as the liquid takes on the temperature of the thermostat, the element is set in operation and the slide given such a position that the telephone is either silent or produces a minimum tone, the intensity of which increases with the least movement of the slide in either direction. In general, the adjustment is made so sharply that the two points on the scale at which an increase of tone may be distinctly recognized are not more than 2 mm. apart. Midway between these two points is the correct position which, after some practice, can easily be determined accurately to from 0.2 to 0.3 mm. The resistances are so inserted that the slide, when adjusted, will lie near the middle of the measuring bridge; an error of 0.3 mm. in the adjustment here will produce an error of about 0.1 per cent. in the value of the conductivity.

Each determination should be repeated by inserting different resistances, and the mean value taken as the basis of the calculation.

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* Kohlrausch, Wied. Ann. 26, p. 175, 1885.

† Kohlrausch, *ibid.* 26, p. 220, 1885.

An indistinctness in the minimum tone may, as already suggested, be due to very different causes. The difficulty is usually removed by replatinizing the electrodes; sometimes an increase in the electrode surface is necessary, varying according to the concentration and nature of the solution, as well as the amount of resistance inserted; frequently also, a more rapid alternation of the current is necessary, and in many cases the cause lies in the amount of resistance. A resistance of from 100 to 1000 mercury units gives, in general, the best results.

After a little practice, ten to twelve solutions may easily be investigated in one-half an hour.

Calculation.—The measurements for chemical purposes are limited almost wholly, in recent times, to the determination of the molecular conductivity represented by the constant μ (or λ, according to Kohlrausch). For the meaning of this constant, see Ostwald, Allgem. Chem., 2. Aufl., Bd. II, p 640, 1893; and Kohlrausch, Wied. Ann. 6, p. 152, 1879, and 26, p. 163, 1885.

μ is calculated from the formula:

$$\mu_v = \gamma \frac{v\,b}{r\,a};$$

or, for aqueous solutions, taking into account the conductivity of the water employed, according to the formula:

$$\mu_v = v\gamma\left(\frac{b}{a\ r} - \frac{b_w}{a_w r_w}\right),^{*}$$

where μ represents the molecular conductivity at the dilution v;

v the volume in liters, which contains one gram equivalent † of the electrolyte;

a and b the lengths of wire to the left and right of the slide;

a_w and b_w the corresponding lengths for water;

r and r_w the resistances in mercury units of the solution and the water;

γ the resistance capacity of the measuring vessel.

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* The formula follows directly from the proportion (p. 59). The correction for the conductivity of water is somewhat uncertain; for solutions of low conductivity the value of μ is doubtful.

† It is better to refer the conductivity to a gram-molecule of the substance, as it is impossible to separate acids, bases, salts, etc., from indifferent substances.

In order to determine the resistance capacity of the vessel,—*i. e.*, the resistance which a liquid with unit conductivity would show in the vessel,—a liquid is used whose conductivity is accurately known. A $\frac{1}{50}$ normal calcium chloride solution which has kept for a long time unchanged has, according to Kohlrausch, a molecular conductivity at 18° of 112.2, and at 25° = 129.7. This value placed in the above formula will give the value of the constant γ. For liquids of low conductivity and narrow electrodes, it is better to take a more accurately investigated solution of low conductivity,—*e. g.*, a solution of tartaric acid.

The molecular conductivity μ at 25° is according to Ostwald *:

v 16	32	64	128	256	512	1024	2048
μ 11.40	16.03	22.47	31.28	43.50	59.51	81.64	109.50.

Other suggestions see Kohlrausch, Wied. Ann. 6, pp. 49 and 50, 1879, and Kohlrausch, Prakt. Phys. VII, p. 304, 1892.

The reduction of the specific conductivity k to terms of μ follows from the relation $\mu = 10^7 k \cdot v$, where μ and v have the meaning given above (Ostwald, Jour. prakt. Chem. N. F. 33, p 353, 1886).

The ratio $\frac{a}{b}$ is given for a wire 1 m. long in the table of Obach. An abbreviated form of this table is given at end of this book.

If the resistance of the wire is not uniform, the wire must be calibrated, and a corresponding correction applied to the above value.

The resistance r also requires a small correction. For most ordinary German-silver wires, an increase of 1° in temperature increases the resistance on an average of 0.0004 parts of the whole value. The necessary reduction to mercury units at 0° is easily made.

If one wishes (which is not always permissible) to establish the value μ_∞,—*i. e.*, the conductivity at infinite dilution,—it is determined indirectly, inasmuch as it does not result from direct observation. Zeit. phys. Chem. 2, p. 843, 1888. For the calculation of the Ostwald constant,—

$$K = \frac{m^2}{(1 - m)\,v} \cdot 100$$

(see Zeit. phys. Chem. 2, p. 278, 1888).

* Ostwald, Zeit. phys. Chem. 3, p. 272, 1889.

The value of μ is usually determined at the temperature 25° (the measurements of Kohlrausch were referred to 18° C.). On the temperature influence or the calculation of the temperature coefficient, see Kohlrausch, Wied. Ann. 6, p. 14, 1879, and 26, p. 222, 1885. If the determinations are made at higher temperatures, the error due to the dissolving of the glass must be taken into account. It is therefore advantageous to boil water in the electrode vessel several times before use. Arrhenius, Zeit. phys. Chem. 4, p. 96, 1889; Krannhals, *ibid.* 5, p. 251, 1891; and Sack, Wied. Ann. 43, p. 212, 1891.

For the calculation of the velocity of ions and the transport numbers from the conductivity, see Kohlrausch, Wied. Ann. 6, p. 160, 1879, and 26, p. 170, 1885; Löb and Nernst, Zeit. phys. Chem. 2, p. 948, 1888; Kistiakowsky, *ibid.* 6, p. 105, 1890; and Bein, Wied Ann. 46, p. 29, 1892.

Instead of the method of Kohlrausch, another method is usually employed in France (Lippman's capillary electrometer, Wiedemann, Elektrizität 1, pp. 468 and 480, 1882; Compt. rend. 83, p. 192, 1876; and Ann. chim. phys. (6) 3, p. 439, 1884, and *ibid.* (6) 23, p. 5, 1891).

Applications of Conductivity.—Organic liquids and their mixtures show such a low conductivity* that this constant, in such cases, is of little significance. The same is true for aqueous solutions of most indifferent compounds; here the imperfect correction for the conductivity of water makes an exact determination very difficult.

For chemical purposes, the conductivity of aqueous solutions of inorganic and also organic salts, acids and bases is of special importance.

1. The constant of molecular conductivity is, to a remarkable degree, a constitutive property, *i. e.*, it depends upon the manner in which the atoms are linked together. Isomeric compounds seldom show equal conductivities. Important discriminations are also possible in stereochemical considerations. On the relation of conductivity to constitution, see Ostwald, Jour. prakt. Chem. N. F. 30, pp. 93 and 225, 1884; 31, p. 433, and 32, p. 300, 1885;

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* Walden, Zeit. phys. Chem. 8, p 434, 1891.

33, p. 352, 1886; Zeit. phys. Chem.: Ostwald, 1, pp. 74 and 97, 1887; 3, p. 170; *ibid.* p. 241; *ibid.* p. 369, 1889; Bethmann, 5, p. 385, 1890; Bader, 6, p. 289, 1890; Walden, 8, p. 453, 1891; 10, pp. 563 and 638, 1892; Berthelot, Compt. rend. 102, p. 46, 1891, and Ann. chim. phys. (6) 23, p. 5, 1891.

2. The determination of the conductivity establishes, in most cases, the basicity of the acid. The difference between the values of μ_{1024} and μ_{32} ($v = 1024$ and 32) amounts to:

for	monobasic	acids	$\Delta =$	about	10
"	dibasic	"	$\Delta =$	"	18–20
"	tribasic	"	$\Delta =$	"	28–31
"	tetrabasic	"	$\Delta =$	"	40
"	pentabasic	"	$\Delta =$	"	50

Walden, Zeit. phys. Chem. 1, p. 529, 1887, and 2, p. 19, 1888, and Ostwald, Zeit. phys. Chem. 2, p. 901, 1888.

3. The remarkable degree to which this constant may be influenced, and the large differences of the same for different compounds makes possible:

(*a*) The determination of the presence of very small quantities of impurities in a definite compound (example, water, p. 67);

(*b*) a very sharp determination of the concentration, often at very high dilutions (Kohlrausch, Ber. d. d. chem. Ges. 24, p. 3560, 1891);

(*c*) the approximate quantitative determination of small quantities of electrolytes in mixtures or solutions with large quantities of substances of rather low conductivity (Fock, Fresen. Zeit. 28, p. 1, 1889, and 29. p. 35, 1890, and Reichert, *ibid.* 28, p. 7, 1889; Arrhenius, Zeitschr. phys. Chem. 9, p. 510, 1892);

(*d*) the determination of the solubility of sparingly soluble compounds in water. (F. Kohlrausch and Rose, Ber. Berl. Akad. 26, p. 453, 1893.)

4. The conductivity is of special interest, on account of its close relation to many other properties; examples: the reaction velocity, dissociation phenomena, freezing point, vapor tension, diffusion, capillarity, viscosity, etc. See:

Ostwald, Grundriss d. allgem. Chem. II, p 363, 1890; also Zeit. phys. Chem. Bd. I–X; van 't Hoff, *ibid.* 1, p. 481, 1887; Arrhenius, *ibid* p. 631.

Measurement of electromotive force: Kohlrausch, Prakt. Phys. VII, p. 311,

1892; Wiedemann and Ebert, Phys. Prakt. I, p. 395, 1890; Ostwald, Lehrb. Allgem. Chem. II, p. 808, 1893; Ostwald, Zeit. phys. Chem. I, p. 403, 1887; Behrend, ibid. II, p. 469, 1893, and Brandenburg, ibid. II, p 552.

Measurement of current-strength: Kohlrausch, Prakt. Phys VII, p. 262, 1892; Wiedemann and Ebert, Phys. Prakt. I, p. 403, 1890; Glazebrook and Schaw, Phys. Prakt. I, p. 387, 1888.

2. CALIBRATION OF A WIRE (Method of Strouhal and Barus).*

Let E (Fig. 31) represent an element, and $A\,M\,B$ the bridge with the wire to be calibrated; I, II, III, IV, V are a number of nearly equal comparison resistances which, for a simple adjustment, are supported in the following manner:

A German-silver wire of suitable thickness and length is divided into n, in figure $= 5$, nearly equal parts, which are soldered into

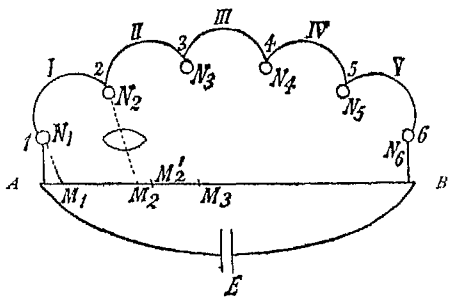

FIG. 31.

short, heavy, amalgamated copper wires. The wires are connected by means of the mercury cups 1, 2, 3 . . . . .; the contacts A — 1 and B — 6 are made by means of heavy copper wires.

The one end N of the wire $M\,N$, which passes through a sensitive reflecting galvanometer, is placed successively in the cups 1 and 2, and the two positions M_1 and M_2 on the bridge, for which the galvanometer shows no deflection, are determined. The wires I and II are then exchanged, so that I is in the position of II, after

* Strouhal and Barus, Wied. Ann. 10, p. 326, 1880.

which the wire $N M$ is placed in 2 and 3, and the positions M'_2 and M_3 determined on the bridge, where the galvanometer shows no current. The wire I is then moved farther up, in that it is exchanged for III; N is immersed in 3 and 4, and the two positions M'_3 and M_4 on the bridge where the galvanometer shows no current is determined.

In this manner the bridge wire is divided into n, in the present case = 5 distances, $M_1 M_2$; $M'_2 M_3$; $M'_3 M_4$ . . . . which, with the above arrangement of the circuit, are all proportional to the same resistance I.

If these lengths of equal resistances are represented in scale divisions by a_1; a_2; a_3 . . . a_n, the mean length

$$= \frac{a_1 + a_2 + a_3 + \dots a_n}{n}.$$

The bridge scale is 1000 mm. in length, and the number of resistances is so chosen that $a = \frac{1000}{n}$ is a whole number; then the values $a_1\ a_2\ a_3$ . . . differ from the calibration interval a only by the very small values $\delta_1\ \delta_2\ \delta_3$ . . .

We have then:

$$\begin{aligned} a_1 &= a + \delta_1 \\ a_2 &= a + \delta_2 \\ &\vdots \\ a_n &= a + \delta_n \end{aligned}$$

and likewise the mean value of the observed resistances:

$$\frac{a_1 + a_2 + \dots a_n}{n} = a + \alpha.$$

Then

$$\alpha = \frac{\delta_1 + \delta_2 + \dots \delta_n}{n};$$

and therefore the correction table for the wire is:

From	$0 - a$	$\alpha - \delta_1$
"	$a - 2a$	$\alpha - \delta_2$
"	$2a - 3a$	$\alpha - \delta_3$, etc.

By summation we have:

For	a	the correction	$\alpha - \delta_1$
"	$2a$	"	$2\alpha - \delta_1 - \delta_2$
"	$3a$	"	$3\alpha - \delta_1 - \delta_2 - \delta_3$, etc.

For exact measurements, instead of five comparison resistances, n is taken equal to 10 or 20. By representing the corrections and the scale divisions graphically, it is an easy matter to determine the correction for any point on the scale. Instead of a constant current and galvanometer it is perhaps better to use an alternating current and telephone.* Large variations in the temperature of the room may occasion errors.†

VII. THE EXPANSION OF LIQUIDS.

The coefficient of linear expansion is the change in length per unit length of a body at 0° for a change of 1° in temperature.

The coefficient of cubical expansion is the change of volume per unit volume at 0° for a change of 1° in temperature.

The coefficient of cubical expansion of a body is very nearly equal to three times the linear expansion $\beta_o = 3\ \beta_l$.

The coefficient of expansion usually increases with the temperature. By the mean coefficient of expansion of a liquid for the temperature interval $t_1 - t$ is meant, the change per unit volume for 1°, on the supposition that the expansion is uniform for each temperature interval. For expansion coefficients see Ostwald, Lehrb. Allgem. Chem., 2. Aufl., Bd. 1, p. 279, 1891.

Expansion of solids, Kohlrausch, Prakt. Phys. VII, p. 95, 1892, and Wiedemann and Ebert, Phys. Prakt., p. 134, 1890.

Expansion of gases, Wiedemann and Ebert, *ibid.* p. 78.

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*Ostwald, Lehrb. Allgem. Chem. II, p. 629, 1893.

[† Closely related to the chapter on conductivities is the determination of the dielectric constant of liquids, which in recent years has become of considerable importance in chemistry. For the determination of this constant see especially method II of Drude, Zeit. phys. Chem. 23, p. 282, 1897.—Tr.]

DETERMINATION OF THE COEFFICIENT OF CUBICAL EXPANSION OF GLASS AND LIQUIDS.

Let s and s_1 represent the specific gravities, v and v_1 the volumes of a liquid at the temperatures t and t_1, and let a represent the coefficient of cubical expansion, then we have the equations:

$$v_1 = v[1 + a(t_1 - t)] \text{ or}$$

$$a = \frac{v_1 - v}{v(t_1 - t)},$$

and likewise

$$a = \frac{s - s_1}{s_1(t_1 - t)}.$$

Hence the coefficient of cubical expansion may be calculated from two determinations of the density or specific volume for the given temperature interval; on the other hand, the values v_1 and s_1 may be calculated if v and s and also a are known.

The coefficient of cubical expansion is usually calculated according to the following equation:*

$$a = 3\beta \frac{p}{p_1} + \frac{1}{t_1 - t} \frac{p - p_1}{p_1},$$

where p and p_1 represent the weights of the liquid contained in the pyknometer (Fig. 32 or Fig. 33)† at the temperature t and the higher temperature t_1; 3β is the coefficient of cubical expansion of glass. If 3β is known, then two weighings of the pyknometer at the temperatures t and t_1 are sufficient for the determination of a.

For ordinary glass 3β can be placed, on an average, equal to 0.000025; for Jena glass, very nearly 0.0000237.

If 3β is to be determined, the pyknometer (Fig. 32 or Fig. 33) is filled with pure mercury and weighed at two different temperatures. If the coefficient of the cubical expansion of mercury is placed equal to 0.000182, then from the above formula we have:

$$3\beta = 0.000182 \frac{p_1}{p} - \frac{1}{t_1 - t} \frac{p - p_1}{p}.$$

* Kohlrausch, Prakt. Phys. VII, p. 97, 1892.

† The pyknometer described in the chapter on Specific Gravity may also be used.

To fill the pyknometer, the point is immersed in recently boiled mercury; by carefully heating and cooling the pyknometer, whereby the mercury is slowly heated to boiling, the vessel is completely filled.

If the pyknometer (Fig. 32) is used, it is placed in a thermostat (p. 65) and heated to two different temperatures.

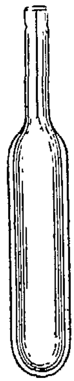
FIG. 32.


FIG. 33.

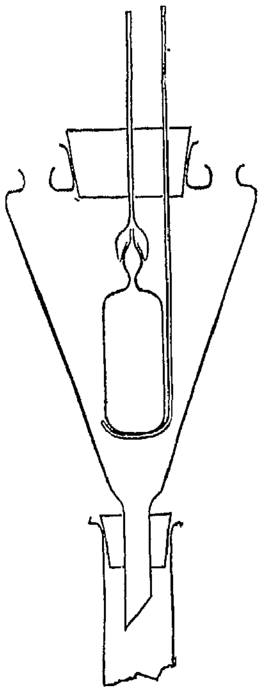
FIG. 34.

The pyknometer (Fig. 33), on the contrary, is heated in the vapor of boiling ether and water in the arrangement shown in figure 34 (= one-half natural size). (Method of R. Schiff.*)

The pyknometer is placed, by means of an iron spoon, in a pear-shaped vessel, which is heated by the vapor of the boiling liquid in

* R. Schiff, Ber d. d. chem. Ges. 18, p. 1539, 1885.

the vessel below. The pyknometer carries a covering with a glass tube, the form of which is shown in the figure, and into which, when lowered, the liquid passes which overflows from the pyknometer. The side openings at the top of the vapor chamber are for a thermometer and a return condenser.

The volume of the pyknometer at 34° is obtained from the weight of the mercury contained in it after heating in boiling ether;* and then by weighing a second time after heating in aqueous vapor, the coefficient of expansion 3β can be calculated. The volume at 0°, v_0 can be approximately calculated from the formula:

$$v_0 = \frac{v_t}{1 + 3\beta \cdot t}.$$

If the coefficient of expansion of the vessel is known, the coefficient of the cubical expansion of the liquid to be investigated is calculated according to page 76. The filled pyknometer is heated in the vapors of liquids adapted to this work.

The determination of the coefficient of the cubical expansion of glass can also be made by the use of the same formula with water free from air. The mean coefficient of expansion of water between the temperatures t and t_1 is calculated † according to the equation:

$$a = \frac{v_1 - v}{v(t_1 - t)} = \frac{s - s_1}{s_1(t_1 - t)}.$$

The pyknometer and method (p. 28) are also applicable.

On the dilatometric method see, among others, Kohlrausch, Prakt. Phys. VII, p. 97, 1890; Lachowitz, Ber. 21, p. 2206, 1888; Bremer, Zeit. phys. Chem. 3, p. 424, 1888; Knöfler, Dissert., Erlangen, 1888, and Thorpe, Jour. Chem. Soc. 63, p. 262, 1893. The pyknometric methods, however, are in general to be preferred.

General.—If the expansion of a liquid is to be established, the coefficients of expansion for different temperature intervals are determined, and the relation of a and t represented by means of equations of the form $a = a + b\ t$ and $a = a + b\ t + c\ t^2$, in which the constants a, b, and c are determined by substituting the corresponding values of a and t.

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* Landolt-Börnstein, Phys. chem. Tabellen, pp. 36 and 37, 1883.

† Landolt-Börnstein, *ibid.* pp. 33–35, 1883.

It is frequently the case that only the specific gravities and specific volumes are given, and the dependence of these two values upon the temperature represented by the interpolation formulas $s_t = s_0\ (1 + a\ t + b\ t^2)$ and $v_t = v_0\ (1 + a\ t + b\ t^2)$, where s_t and v_t represent the specific gravity and volume at $t°$, and s_0 and t_0 the corresponding values at 0°. The calculation of the constants is best made by the method of least squares.* The true coefficient of expansion then is:

$$\frac{1}{v_0} \cdot \frac{d\,v}{d\,t} = a + 2\,b\,t + \ldots$$

Frequently the calculation is made according to the formula of Mendelejeff:

$$v_t = \frac{v_0}{1 = k\,t},$$

in which k is a characteristic constant which can be determined by substituting the values of v_0, v_t, and t. The results, however, from this formula do not agree in all cases. Konowalow, Zeit. phys. Chem. 1, p. 39, 1887, and 2, p. 1, 1888; Grimaldi, *ibid.* 1, p. 550, 1887, and 2, p. 374, 1888, and Heilborn, *ibid.* 6, p. 578, 1890, and 7, p. 367, 1891. *Ibid.*, see tables of the expansion of organic liquids; for tables of the expansion of salt solutions see Gerlach, Spez. Gewichte der Salzlösungen, Freiburg, 1859, and Tschernai, J. russ. Ges., pp. 430 and 486, 1888; reference, Zeit. phys. Chem. 4, p. 483, 1889.

VIII. THE MELTING POINT AND SOLIDIFYING POINT.†

Method I.—For large quantities of substance use is made of the following arrangement:

A cylinder about 3 cm. wide, which is provided with a carefully

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* Kohlrausch, Prakt. Phys VII, p. 10, 1892.

† Landolt, Zeit. phys. Chem. 4, p. 353, 1889.

tested thermometer and a stirrer, and containing at least 15 to 20 gm. of the substance, is placed in a large beaker glass which contains a suitable heated liquid (water, concentrated solutions of sodium chloride or calcium chloride, paraffin, oil).

The hot liquid is heated for some time to a temperature above the probable melting point, estimated, if necessary, by a previous investigation of the substance. As soon as a portion of the substance is melted, the stirrer, a glass rod bent into a glass ring, is moved constantly. If a thermostat with a stirring arrangement * is used instead of an ordinary water-bath, the temperature may be regulated still more accurately.

The thermometer (as long as sufficient quantities of solid substance is found with the molten material) is kept at a constant temperature for several minutes, or for a longer time when larger quantities of material are used. The necessary corrections to the observed melting point (due to the thread of mercury which projects above the surface, etc., must not be neglected; an accuracy of 0.1° C. or less may be easily attained.

The solidifying point which comes into question, especially with mixtures of substances, is determined in the same apparatus.

After melting the substance the temperature of the surrounding water-bath (thermostat) is kept constant for some time at from 1 to 2° below the melting point of the substance. By throwing a small crystal into the molten substance, the solidification is brought about and the temperature is then read off. The determination of the solidifying point requires that the temperature be held constant for a longer time, and, in general, that larger quantities of material be used than for the determination of the melting point. Twenty gm. are here scarcely sufficient.

By using from 100 to 1000 gm. of substance, the melting point as well as the solidifying point can be kept constant for an hour.

The least impurities frequently have great influence on the melting point; the substances should therefore be carefully purified.

Substance for investigation: Naphthalene, melting point = solidifying point = 80.03° C.

Method II.—It frequently happens that only a small quantity

* Page 65, and Küster, Zeit. phys. Chem. 8, p. 578, 1891.

of the substance can be had for the investigation. In such cases it is better to make use of the following much used but inaccurate method for determining melting points:

A vessel *A* (Fig. 35) is filled to the height shown in the figure with pure concentrated sulphuric acid, in which is immersed a thermometer on which is fastened, by means of platinum foil and platinum wire, a capillary tube closed at the lower end; the two are so joined that the small portion of substance introduced into the bottom of the small tube lies in the immediate vicinity of the mercury bulb of the thermometer.

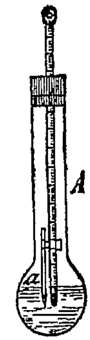

FIG. 35.

The vessel is slowly and carefully heated, and the temperature at which the substance begins to melt away from the walls of the tube is taken as the melting point. The values observed for the melting point show variations of from 1 to 2°, depending upon the width of the tube; with very narrow tubes the results are too high. The results are somewhat concordant if the tubes used are always of the same diameter, about 1.5 mm. at the lower part.

IX. DEPRESSION OF THE FREEZING POINT OF SOLUTIONS.

Principle.—The freezing point of the solvent and the solution of known concentration are determined; the difference between these two temperatures is the depression of the freezing point, from which the molecular weight of the dissolved substance may be calculated according to page 89.

1. METHOD OF BECKMANN.*

Apparatus (Fig. 36).—The inner tube *A*, which is provided with a thermometer and stirrer, and also a side tube, contains the liquid, the freezing point of which is to be determined.

* Beckmann, Zeit. phys. Chem. 2, pp. 638 and 715, 1887, and 7, p. 323, 1891.

A is fastened by means of a cork in the wider tube *B*, which in turn is supported, by means of a metallic cover, in the outer glass vessel *C* (from 2 to 3 l. capacity).

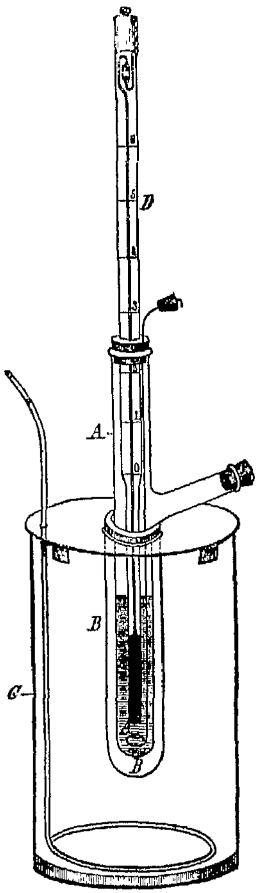

FIG. 36.

The vessel *C*, which is provided with a stirrer, contains the freezing mixture. Between *B* and *A* is a layer of air which separates the liquid to be frozen from the freezing mixture, and consequently allows the liquid to cool uniformly and gradually.

For accurate determinations the thermometer must be graduated to $\frac{1}{50}$ or $\frac{1}{100}$ of a degree. A Beckmann thermometer is well adapted to this work. The mercury reservoir at the top is so large that the thermometer will also answer for determinations according to the boiling point method. The stirrer for the inner vessel should be made of platinum; a ring of platinum foil is soldered to a thick platinum wire. A glass stirrer, however, may be used without any special disadvantage.

If the inner vessel is to be closed at the top, the stirrer may be moved through a cork or rubber stopper.

Method of Operation.—For accurate determinations the apparatus should be set up in a room, the temperature of which differs not more than one degree from the freezing point of the solvent. A temperature difference of 10° may influence the depression of the freezing point as much as 0.01°.

The temperature of the freezing mixture should be from 3 to 4° below the freezing point of the liquid to be investigated. The result is influenced if the temperature for one observation is allowed to vary more than 1 to 2° from that of the other observations with the same solvent and solution.

For aqueous solutions, suitable mixtures of snow or ice and salt water may be used for cooling; when working with benzene (melting point about 5.4°) a mixture of water and ice is sufficient, regardless of the concentration of the solution; for acetic acid (melting point 16.7°) the temperature of the surrounding water may be lowered by means of small pieces of ice; for solutions in phenol (solidifying point 40° to 41°) and naphthalene (solidifying point 80.0°), use is made of a thermostat (p. 65) or a beaker glass, by means of which the solidifying point of the molten substance may be determined according to page 79.

The freezing point of the solvent is determined in the following manner:

Tube *A* is provided with a sharp-edged piece of platinum, tared, and supplied with about 15 gm. of the solvent, so that the upper part of the tube remains dry. The quantity of solvent is then accurately weighed to one centigram.

After placing in the apparatus the liquid, during constant stirring, is cooled to near the freezing temperature, and the freezing induced by means of a crystal of the solvent. The thermometer falls usually several tenths of a degree below the freezing point, rises immediately after the beginning of the crystallization, and after thirty to sixty seconds—with sufficient separation of ice—attains a maximum which is taken as the freezing point of the solvent.

The degree of over-cooling may slightly influence the accuracy of the result (to 0.02°); the over-cooling, therefore, for the parallel observations with the solution and solvent should be regulated as uniformly as possible (about 0.1° below the freezing point). This is usually accomplished by introducing the ice crystal which induces the freezing, at correspondingly equal temperature intervals from the freezing point. For water and dilute aqueous solutions it is desirable that the over-cooling should be 0.5°, on account of the otherwise insufficient separation of ice; for concentrated aqueous solutions, on the other hand, the over-cooling must not be more than 0.2°.

If acetic acid is used, its hygroscopic properties must be taken into consideration for accurate determinations. Tube *A* is then provided with a stopper. The error, however, introduced by the

absorption of water amounts to scarcely more than 0.01° in the reading of the thermometer.*

The solvents, especially acetic acid, benzene, and others should be used only in a pure condition.

After determining the freezing point of the solvent, which should be done before and after each series of observations, the substance to be dissolved is introduced through the side tube into the tube *A*.

Solids are weighed off in small glass tubes, by means of which they are introduced into the solvent, or they may be introduced in

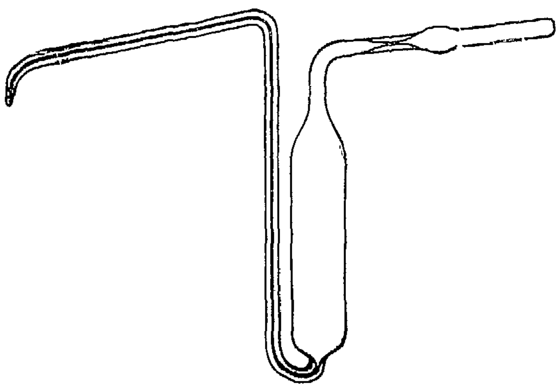

FIG 37

the form of pastilles, which are prepared by means of a pastille-press.

For the introduction of liquids, the pipette (Fig. 37) may be used. By means of this arrangement the liquid is blown into the freezing tube. If the capillary tube is very thin-walled and ground off sloping at the outlet, no drop will remain hanging; the pipette then needs only to be weighed before and after the removal of the liquid. The determination of the freezing point of the solution follows, just as for the pure solvent.

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*The use of the recent complicated apparatus of Beckmann (Zeit. phys. Chem. 7, p. 324, 1891) is unnecessary in this case. For difficultly soluble substances the solution is prepared (if necessary with exclusion of the outer air), and observed according to the method of Raoult (p. 86).

The introduction of crystals to induce the freezing is, especially during the warm months, attended with difficulty. Small crystals melt too quickly and larger crystals give rise to too great a change in concentration. Beckmann recommends for that purpose the contrivance ("Impfstift") represented in figure 38.

A portion of the liquid in A is sucked up into the narrow tube B, which is open at the lower end and closed at the upper end by means of a pinch-cock, and the whole placed in a freezing mixture and brought to freezing. B is then removed from A, and the substance thawed a little by slightly warming the walls of the tube at the bottom and afterward above. A momentary opening of the pinch-cock C is sufficient to remove the cylindrical substance from the open end of the tube. The small quantity of projecting substance may be brought into the freezing liquid by means of the stirrer.

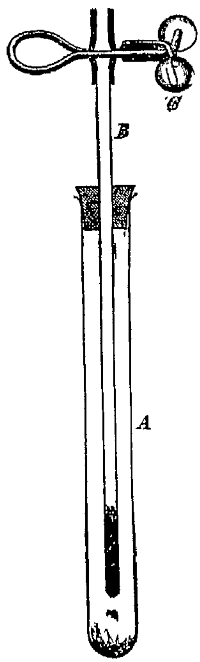

FIG. 38

The method of Beckmann is used if an approximate determination of the molecular weight is desired; the limit of accuracy is about five per cent. of the calculated value of the molecular weight. The change of concentration gives rise to errors; over-cooling of more than 0.1° is, therefore, especially for concentrated solutions, to be avoided.

An advantage of the method is the small quantity of substance required for a molecular weight determination.

Inasmuch as a concentration which lowers the freezing point from 0.05 to 0.1° can be investigated, a $\frac{1}{10}$ per cent. solution, corresponding to one centigram of the dissolved substance, is sufficient for carrying out a molecular weight determination.

2. METHOD OF RAOULT.

This method is employed for all accurate determinations. A thick-walled open beaker of 120 to 150 c.c. capacity is placed in the vessel containing the freezing mixture.

The (Beckmann) thermometer is so placed in the middle of the glass vessel that no ice freezes on the lower end of the mercury reservoir situated near the bottom of the vessel. The stirrer consists of platinum foil and heavy platinum wire soldered together.

The quantity of liquid employed should always be the same, from 100 to 120 c.c. The solutions are previously prepared by weighing—with the greatest possible exclusion of air in the case of acetic acid. Each solution should be used only for one observation; the freezing point of the pure solvent is determined before and after each series of experiments.

The temperature of the freezing mixture should always be kept constant to within 1°; this temperature should be from 3 to 4° below the freezing point of the liquid. The temperature of the room should be, at most, not more than 5° above the freezing point of the solvent. Especially does the temperature of the room influence the result if, as with water, the ice separates as a solid cylinder on the glass. The error in such cases, for rather high temperatures of the room, may amount to 0.02°.

The over-cooling should be as uniform as possible—about 0.05 to 0.1°; only for water and its dilute solutions, in order to obtain loose and finely divided ice, should this value amount to 0.5°. The freezing is induced by the introduction of an ice crystal at a temperature very near the freezing point, or about 0.1° above.

The temperature is read off by means of a microscope accurately to 0.002°.

The more concentrated the solution, the more rapidly the thermometer thread sinks, on account of the change of concentration due to the separation of ice. A small error is also introduced with concentrated solutions for the highest position of the mercury thread. The value of the necessary correction may be determined by observing, from minute to minute, the sinking of the mercury thread for solutions of different concentrations, for a period of ten to twenty minutes, and then calculating the time consumed from

the beginning of the separation of ice to the reading of the highest position of the mercury thread. This correction is sufficient, inasmuch as it is usually very small (at most 0.01 to 0.02°), and really not so large as would be expected from the quantity of ice separated out.

The liquid, during the separation of the ice and previously, must be well stirred. If a large number of determinations are to be made, the use of Raabe's turbine (p. 65) is recommended. The stirrer is moved in a vertical direction.

If aqueous solutions are to be investigated in midsummer when the temperature of the room is considerably above 0°, sufficient quantities of loose ice are formed in the liquid in that the mercury reservoir of the thermometer is loosely surrounded by a platinum or silver net, and the thermometer fastened to a turbine (with the necessary care) is set in rapid motion

By exercising considerable care, the depression of the freezing point may be determined, by this method, accurately to from $\frac{1}{1000}$ to $\frac{2}{1000}$ of a degree; the further complications of the method (Raoult, Compt. rend. 114, p. 218, 1892, and Zeit. phys. Chem. 9, p. 343, 1892, as well as Loomis, Ber. d. d. chem. Ges. 26, p. 797, 1893) may be omitted.

According to Jones (Zeit. phys Chem. 11, pp. 110 and 531, 1893, as well as Ber. d. d. chem. Ges. 26, p. 547, 1893) it is advantageous, for a high degree of accuracy, to experiment with at least one liter of solution; also to make use of a thermometer graduated to $\frac{1}{1000}$ degree.*

Choice of Concentration and Solvent for Freezing Point Determinations.—The determinations in general, especially molecular weight determinations, should not be limited to a single concentration. After investigating various concentrations and noting the calculated molecular weight as well as the concentrations in a system of coördinates, certain reference points regarding the molecular weight of the dissolved substance are obtained; especially if the investigations are to be extended to dilute solutions. By the method of Beckmann, using always the same

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* [See also the investigations of Loomis, Wied. Ann. 51, p. 500, 1894; 57, p. 495, 1896; 60, 523, 1897, and Ber. d. d. chem. Ges. 26, p. 794.—Tr.]

quantity of solvent, the concentration of the solution to be investigated is successively increased by the addition of small quantities of substances through the side tube (Fig. 36) into the thawed solution.

Care should also be exercised in choosing the solvent, especially for molecular weight determinations. In doubtful cases the investigation should be made with several solvents.

Water may be used, so far as the conditions of solubility admit, excellent as solvent for organic compounds of an indifferent nature (not conductors). Considerable care is necessary for acids, bases, and salts; also for certain organic compounds (especially for high dilutions) the molecular weight found is too large.

Acetic acid has perhaps the most general application. The constants are here much less dependent upon the concentration than with other solvents; the calculated values for the molecular weights are usually normal

The following solvents may be used with similar results: formic acid, lauric acid, stearic acid, thymol, phenol, etc.

The acid character of these solvents, however, must always be taken into account.

Benzene, which can be used only in the purest condition, is well adapted on account of the relatively large depression which is produced, even by dissolving a minimum quantity of substance.

However, substances dissolved in this solvent have a special tendency to form more complex molecules, which are broken up only at high dilutions; even then, values calculated for the molecular weight are sometimes too large.

This is especially true for compounds containing the hydroxyl group, particularly hydroxyl compounds of acid nature.

Similar to benzene may be mentioned the solvents nitro-benzene, ethylene-dibromide, and naphthalene; the high melting point and strong dissociative properties of the last-named compound must be taken into consideration.

In regard to the influence of concentration and solvent on the freezing point and molecular weight, see, among others, Arrhenius, Zeit. phys. Chem. 2, p. 491, 1888; Beckmann, *ibid.* 2, p. 715; Fabinyi, 3, p 39, 1889; Magnanini, *ibid.* 3, p. 347, 1889; Eykman, *ibid.* 4, p. 487, 1889; Paterno, *ibid.* 5, p 94, 1890, abstract.

On the use of Beckmann's apparatus for solvents which do not solidify, see Nernst, Zeit. phys. Chem. 6, p. 573, 1890; also F. Bauke, The Raôult Freezing Method and its Use for Chemical Investigations, Berlin, 1890. For substances suited for these investigations, see references already cited.

CALCULATION OF MOLECULAR WEIGHTS.

The calculation of the molecular weight from the depression of the freezing point is based upon the empirical facts established by Raoult and the thermodynamical considerations of van 't Hoff,* according to which one molecule of any substance dissolved in a definite quantity of a solvent lowers the freezing point of the solvent by a constant quantity.

According to Raoult, the characteristic constant for each solvent may be calculated from the equation:

$$\frac{ME}{P} = C.$$

M is the molecular weight of the dissolved substance, E the depression of the freezing point, P the number of grams of substance contained in 100 gm. of solvent, and C is the characteristic constant (the molecular depression).

According to van 't Hoff, we have:

$$\frac{ME}{p} = \frac{0.02\ T^2}{W}.$$

M and E have the same values as above, p represents the number of grams of dissolved substance contained in 100 gm. of solution (not solvent), T is the absolute melting point of the solvent, and W the heat of fusion of the solvent.

The constants C and $\frac{0.02\ T^2}{W}$ are found to be very nearly equal.

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* van 't Hoff, Zeit. phys. Chem. 1, p. 497, 1887.

The mean values calculated for C and $\frac{0.02\ T^2}{W}$ are as follows:

Solvent		C	$\frac{0.02\ T^2}{W}$
Water,	=	18.5	18.9
Acetic Acid,	=	38.6	38.8
Benzene,	=	50.0	53.0
Phenol,	=	74.0	76.0
Naphthalene,	=	69 0	69.4
Formic Acid,	=	27.7	28.4
Nitro-benzene,	=	70.7	69.5
Ethylene-bromide,	=	118.0	117.0*

The calculation of the molecular weight is usually made by substituting the values of the constant $\frac{0.02\ T^2}{W}$ in the formula of van 't Hoff.

On the relation of the freezing point to the electric conductivity, and the calculation of the van 't Hoff coefficient i from the freezing point, see, among others, Zeit. phys. Chem. 1, pp. 497 and 633, 1887, and 2, p. 491, 1888. Application of the freezing and boiling method, see page 108 of this work.

X. THE BOILING POINT AND VAPOR PRESSURE.

General.—The normal boiling point is the temperature of the vapor which rises from the liquid boiling under a pressure of 760 mm. of mercury.

In the broader sense, the boiling point is the temperature at which the vapor pressure of the liquid is great enough to overcome the external pressure.

The boiling point, therefore, is a function of the external pressure.

* Constants for other solvents see, among others, Eykman, Zeit. phys. Chem. 4, p. 515, 1889, and Raoult, Compt. rend. 95, pp. 188 and 1030, 1882.

Distinction between the static and dynamic methods is made according as the pressure of a vapor above its liquid is measured at different temperatures, or the boiling temperature determined which corresponds to a definite pressure.

In general, the determination of the normal boiling point is sufficient.

1. ORDINARY METHOD FOR THE DETERMINATION OF BOILING POINTS.

The three forms of apparatus (Figs. 39–41) are especially applicable for boiling-point determinations.

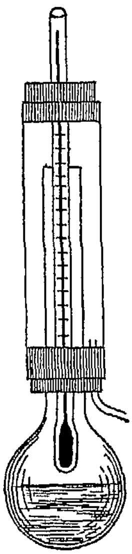

FIG. 39.

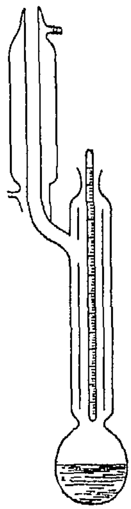

FIG. 40.

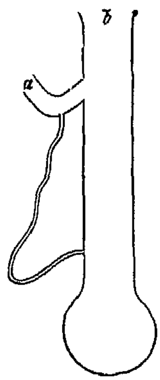

FIG. 41.

Figure 39 represents the arrangement of Berthelot.* An outer wide tube surrounds the neck of the flask in which the thermometer is placed. The flask is connected with a simple condenser.

* Berthelot, Méc. chim., Bd. I, p. 288, 1879.

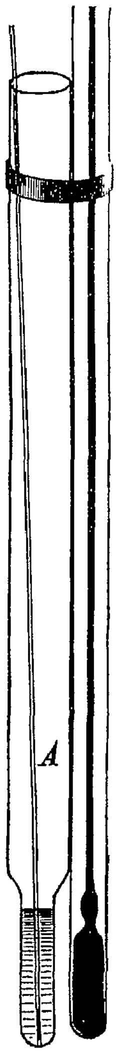

FIG. 42.

The apparatus figure 40 (O. Schumann *) has the advantage of being made entirely of glass.

The flask figure 41 (L. Meyer) is provided with a return condenser at *a* and a stopper and thermometer at *b*. The narrow side tube has an arrangement to prevent the liquid which flows back in the cooler from coming in contact with the thermometer.

The thermometer, which has been carefully tested, (see under 3, chap. xx), is, whenever possible, introduced into the vapor chamber so far that the correction for the projecting thread of mercury may be neglected.

The bumping of liquids should be prevented. This may be done by throwing in small pieces of platinum or some porous clay or soap-stone; also by means of a capillary tube in the stopper, through which a slow current of gas is conducted into the boiling liquid. Also by the arrangement on page 98.

The barometric pressure (4, chap. xx) must always be observed simultaneously with the determination of the boiling point.

If the barometric pressure is b mm. of mercury, the boiling point at 760 mm. is obtained very closely by adding $0.0375\ (760 - b)$ degrees to the observed temperature.

If the boiling point is to be determined accurately to the $\frac{1}{100}$ of a degree, the method should be carried out as described on page 97 and following; and the Beckmann apparatus (p. 104) should be employed. See also the simple apparatus of Glazebrook and Shaw, Physik. Prakt., p. 183, 1888.

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* Schumann, Ber. d. d. chem. Ges. 18, p. 2086, 1885.

2. DETERMINATION OF THE BOILING POINTS OF LIQUIDS IN SMALL QUANTITIES.

(*a*) METHOD OF SIWOLOBOFF.*

The glass tube *A* is fastened to a thermometer as shown in figure 42, and in it is placed one or two drops of the liquid whose boiling point is to be determined.

In *A* is a capillary tube which may be prepared by drawing out a wider tube. The drawn-out portion is fused together in the middle and then (see figure) broken off above the place melted together.

If the apparatus is placed in an outer temperature-bath (glycerin, water, sulphuric acid), small bubbles are produced in the capillary tube before the boiling begins; these bubbles are quickly increased to a uniform chain of small vapor bubbles. The corresponding temperature is taken as the boiling point. Errors of 0.5 to 1° are liable to occur with this method.

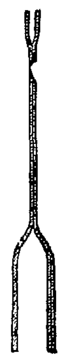
FIG. 43.

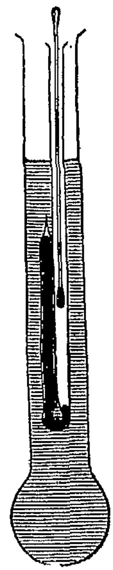
FIG. 44

(*b*) METHOD OF JONES-SCHLEIERMACHER.†

By this—static—method, the temperature is determined at which the vapor pressure of the substance is equal to the atmospheric pressure. This temperature is the boiling point of the substance for the given pressure.

A U-shaped barometer tube is formed from a clean, dry, glass tube of about 50 cm. in length and 6–8 mm. in width, as shown in figure 44, so that the shorter limb ends in a hair-like capillary opening as in figure 43.

About one decigram of the liquid or solid substance is introduced

* Siwoloboff, Ber. d. d. chem. Ges. 19, p. 795, 1886.

† Schleiermacher, Ber. d. d. chem. Ges. 24, p. 944, 1891, and Jones, *ibid.* p. 2251.

into the dry tube through the opening of the longer limb. By inclining the tube (after heating a solid substance until liquefied) the substance can be conducted over into the shorter limb. Dry mercury is then allowed to flow in slowly until it stands, in both limbs, about 2 cm. below the closed end; in this way the liquid or liquefied substance is collected above the mercury in the short limb. A portion of the substance which may remain in the longer limb will have no influence on the result. The liquid is then heated to faint boiling until the air clinging to the walls of the tube or absorbed by the liquid is completely removed through the capillary opening. Mercury is then carefully introduced until the liquid fills the shorter limb up to the wider portion of the capillary. The fine capillary tube is then melted off by means of a small pointed flame. Only a small gas-bubble remains then in the point of the capillary tube, the influence of which on the accuracy of the result may be neglected.

The mercury in the open limb is then removed down to the upper end of the bend in the tube, by simply inclining the U-tube downward to a horizontal position. If the tube is narrowed somewhat at the bend, the entrance of air-bubbles into the closed limb is prevented.

The apparatus with a thermometer is then fastened in the (not too narrow) pear-shaped vessel of V. Meyer. The thermometer is placed as shown in figure 44. The liquid bath may be water, sulphuric acid, paraffin, etc.

The apparatus is slowly heated, and the use of a stirrer is advantageous.

The temperature at which the mercury assumes the same height in the two limbs is the boiling point for the atmospheric pressure.

If the thermometer is reliable, and the mean of several observations is taken (also by cooling the hot liquid to the boiling temperature), an accuracy of from 0.2–0.3° may be attained by this method.

3. DETERMINATION OF THE BOILING POINT AT. DIFFERENT PRESSURES.

In order to establish the relation between the vapor pressure and the boiling temperature, the dynamic method is preferable.

A boiling-vessel, as represented in figure 40 or figure 41, is connected with an air-tight pressure regulator.

A simple form of apparatus* is represented in figure 45.

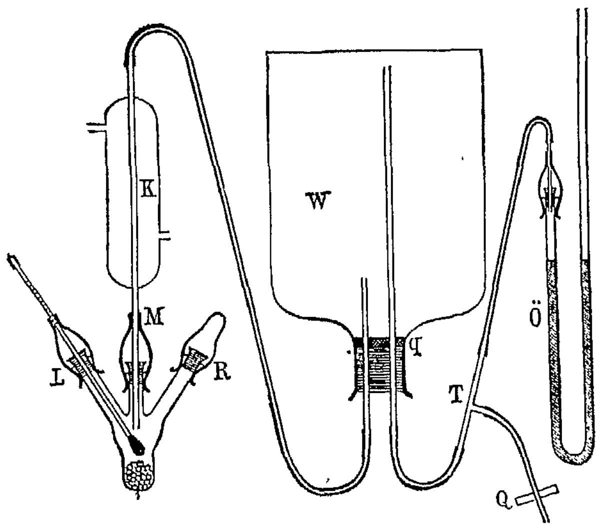

FIG. 45.

The Beckmann boiling apparatus described on page 98 (which can be made air-tight by closing the boiling apparatus) is connected through the cooler *K* with the air-chamber *W* and the manometer *Ö*. At *T* is a branch tube with a pinch-cock *Q*, which connects the apparatus with an air-pump or gas generator, so that the pressure in the apparatus can be increased or decreased at pleasure.

The manometer is filled with pure, clear sweet oil, the specific gravity of which (for different temperatures) has been determined.

The air-chamber *W*, which is interposed for the adjustment of

* Roloff, Zeit. phys. Chem. 11, p. 25, 1893.

small pressure-fluctuations in the apparatus, has a capacity of at least 12 l. If the manometer still shows irregular variations, a capillary tube 10–20 cm. long is inserted.

The closing of the apparatus absolutely air-tight from the outer air is accomplished (1) by surrounding the stoppers of the manometer and boiling apparatus *L M R* with rubber capsules fastened by means of wire; (2) by connecting the glass parts with thick-walled rubber tubing; and (3) by placing a layer of mercury *q* at the top of the cork in the air chamber.*

The regulator is protected from the heat by placing a screen between it and the boiling apparatus.

A cathetometer (2, chap. XX) is used in reading the manometer and thermometer; fluctuations in frequent readings of barometric pressure are to be taken into account. In order to eliminate the influence of the possible barometric variations, it is better to determine the boiling point at normal pressure before and after each series of observations.

Before making the experiment, the apparatus should be tested for its air-tightness by varying the internal pressure. Liquid for investigation, water, see Landolt-Börnstein's Tabellen, p. 47, 1883; also Schmidt, Zeit. phys. Chem. 7, p. 433, and 8, p. 628, 1891; *ibid.* 7, p. 441, boiling apparatus with pressure regulator.

Other pressure regulators, see L. Meyer, Lieb. Ann. 165, p. 303; Städel and Hahn, Lieb. Ann. 195, p. 218, and Ber. d. d. chem. Ges. 13, p. 839, 1880; O. Schumann, Wied. Ann. 12, p. 44, and Ber. d. d. chem. Ges. 18, p. 2086, 1885; Brown, Phil. Mag. (5) 7, p. 411, Perkin, Jour. Chem. Soc., p. 689, 1888, and Obach, Zeit. f. angew. Elektr. von Carl, p. 69, 1880.

Apparatus for the static method, see Schmidt, Zeit. phys. Chem. 8, p. 629, 1891; Kahlbaum, Ber. d. d. chem. Ges. 19, p. 2954, 1886; Bremer, Rec. Pays-Bas 6, p. 121, 1887; Emden, Wied. Ann. 31, p. 145, 1887; Tammann, Akad. St. Petersburg, Mém. 35, Nr. 9, 1887; Ref. Zeit. phys. Chem. 2, p. 42, 1888; Raoult, Zeit. phys. Chem. 2, p. 354, 1888; Beckmann, *ibid.* 4, p. 532, 1889.

The relation of pressure and temperature is represented graphi-

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* The apparatus may also be made air-tight by means of rubber stoppers.

cally, or expressed by interpolation formulæ of the form, $\log E = a + b\,a^t$ and $\log E = a + b\,a^t + c\,\beta^t$ (Ostwald, Lehrb. Allgem. Chem., 2. Aufl., Bd. 1, p. 313, 1891, and Schmidt, Zeit. phys. Chem. 7, p. 444, 1891).

Relation of the boiling point to the constitution of organic compounds, see Marckwald, Verlag von Friedländer & Sohn, Berlin, 1887.

Tables of vapor pressures of solutions, see, among others, Tammann, Ref. Zeit. phys. Chem. 2, p. 42, 1888.

Critical temperature and pressure. Method of determination.

Pawlewski, Ber. d. d. chem. Ges. 15, p. 2460, 1882, and Schmidt, Lieb. Ann. 272, p. 273, 1891.

Galitzine, Wied. Ann. 41, p. 614; Cailletet and Colardeau, Compt. Rend. 112, pp. 563 and 1170, 1891; Altschul, Zeit. phys. Chem. 11, p. 577, 1893, and Battelli, Ann. chim. phys. 29 (6), p. 400, 1893; Tables of critical data, Heilborn, Zeit. phys. Chem. 7, p. 602, 1891; *ibid.* complete literature.

XI. ELEVATION OF THE BOILING POINTS OF SOLUTIONS.

Principle.—The boiling points of the solvent and the solution are determined in a suitable apparatus, and, from the elevation of the boiling point thus found, the molecular weight of the dissolved substance is calculated according to the formula on page 107.

1. METHOD I OF BECKMANN.*

This method finds special use when the boiling point of the solvent is less than 100° (at the highest 130°).

Apparatus.—The boiling-vessel consists of a three-tubed glass flask *A*, as shown in figure 46.

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* Beckmann, Zeit. phys. Chem. 4, p. 533, 1889, and 6, p. 437, 1890.

In the one tube is fastened a Beckmann thermometer, graduated to $\frac{1}{50}$ or $\frac{1}{100}$ of a degree, by means of a tightly fitting cork. In the middle tube *b* is introduced the reflux tube from the condenser

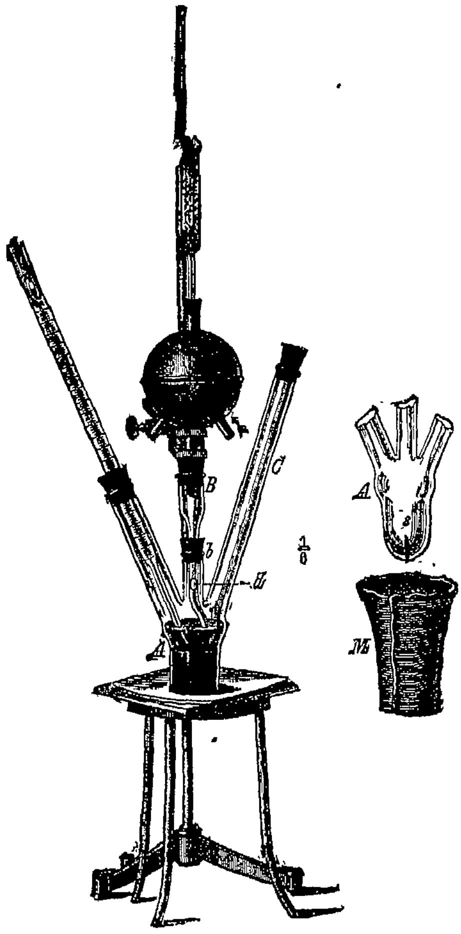

FIG. 46.

B, which can be employed, for most liquids, in the form given by Soxhlet; the opening at the top of this metallic cooler is provided with a calcium chloride tube, which is filled with not too finely

divided granules of perfectly anhydrous calcium chloride. The lower part of the tube from the reflux condenser is provided at *d* with a vapor-hole, which is situated in the vapor chamber, and through which the evolved vapor rises to the condenser. The tube *C*, which is closed with a cork during the investigation, serves for the introduction of the substance into the boiling solvent.

In order to protect the apparatus from side-heating, it is placed in an asbestos jacket *m*, which can be protected at the top from the heat influence of the surrounding air by covering over with clay. This jacket, with the boiling-apparatus, for further protection against the flame, rests on two asbestos plates; in the middle of the upper one is a hole, the diameter of which is equal to that of the asbestos jacket.

To prevent the liquid from bumping, a short piece of thick platinum wire *s* is fused into the bottom of the boiling-vessel; whereupon the boiling takes place uniformly with the formation of small bubbles of vapor only at the surface of this wire, owing to its greater conductivity of heat.

The boiling-vessel is filled to the middle with glass-wool or glass pearls 3 to 4 mm. in diameter. Through the introduction of these, previously cleaned with con. hydrochloric acid, the temperature is regulated uniformly in the interior of the liquid, and overheating is avoided. The subsequent cleaning of the pearls, in case the substance has adhered closely, is best accomplished in Soxhlet's extraction apparatus.

The substance to be dissolved is introduced, during the boiling, through the opening in the tube *C*, which is opened and closed as quickly as possible; whereby the evaporation, even for highly volatile solvents (as ether), is scarcely perceptible on account of the length of the tube.

Substances which are easily liquefied are blown into the solvent by means of a pipette of the form represented in figure 47.

The pipette is suitably graduated in cubic centimeters, and, when necessary, is provided with a calcium chloride tube. The pipette is introduced into the tube *C*. Before reweighing, the liquid is sucked back out of the capillary tube.

Viscous liquids may be introduced into the apparatus by means of the valve-tube represented in figure 48.

This tube, filled with the substance, is weighed and allowed to slide through the tube *C* into the solvent. At the bottom of the boiling-vessel the valve at the lower end of the tube opens and allows the liquids to mix.

As far as possible, the introduction of glass into the boiling-vessel is to be avoided, inasmuch as any change in the level of the liquid in the boiling-vessel influences the vapor pressure and the boiling point of the liquid.

The raising of the level 1 mm. corresponds to 0.002° in the elevation of the boiling point. The introduction of several tubes, as well as larger quantities of dissolved substance, will produce a small error by decreasing the volume of the vapor-chamber.

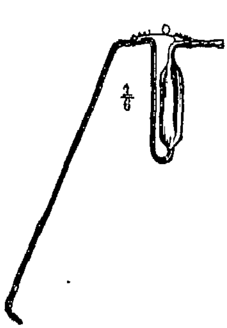

FIG. 47.

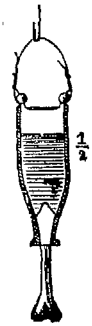

FIG 48.

It is undesirable, therefore, to introduce solid substances in a vessel. Powdered substances are made into pastilles, the size of which depend upon the solubility of the substance (Pharm. Centralhalle 30, p. 132, 1889).

Method of Operation.—The boiling-vessel, together with its pearls, is tared on a balance which weighs accurately to 1 cgm.; it is then filled with the pure solvent to the height indicated in the figure, and the quantity of the same determined by weighing.

Inasmuch as, for not too violent boiling, the temperature of the vapor and the pure solvent are the same in this arrangement, the thermometer is so inserted that the mercury reservoir is completely covered with the liquid without coming in contact with the pearls.

The lower part of the tube from the reflux condenser is bent to

one side, and is fastened in the boiling-vessel so that the lower portion is removed as far as possible from the thermometer, thereby preventing any direct influence, of the somewhat cooler liquid flowing back, on the reading of the thermometer. The lower end of each tube immersed in the liquid stands about 1 cm. from the pearls; hence the back-flow is not hindered through the evolution of vapor-bubbles.

The prepared boiling-vessel, after being wrapped with asbestos, is heated by means of a Bunsen burner. For ethereal solutions the point of a luminous flame is used; for alcohol, etc., the non-luminous flame of the burner is employed. If the asbestos packing is properly adjusted, the difference in the highest reading of the thermometer for ether heated with the small point of the flame and the full Bunsen flame amounts to, at most, 1° C. In general, it is important in the investigation of a solvent and its corresponding solution that the size of the flames should be as nearly as possible the same in the two cases. The use of a regulator-cock or the membrane gas pressure regulator of Elster * is advantageous, if not indispensable. Investigations in the evening should be avoided, on account of the irregular gas pressure at that time.

The boiling should be so regulated that for ether and carbon-disulphide, one drop every two to five seconds, for alcohol, benzene, or acetic acid, one drop every five to ten seconds, falls from the condenser at *B*.

The boiling is then made somewhat more vigorous by means of a larger flame; if, however, the boiling point has been reached or passed, the liquid is cooled to one-tenth of a degree below the boiling point and again heated, so that there is always a moderate boiling. After a time, the mercury assumes a constant position, which can be taken as the boiling point (of the solvent) only when it remains constant to 0.002° for at least five to ten minutes. The thermometer should always be gently tapped before reading off the temperature, as this frequently produces a slight change in the position of the mercury. The boiling point should always be determined by allowing the mercury thread in the thermometer to

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* Beckmann, Zeit. phys. Chem. 4, p. 546, 1889.

rise, as the definite positions of the mercury attained through the rising and falling of the thread show small variations.

After reading off the boiling point, without removing the flame, a weighed quantity of substance is introduced through *C* into the boiling-vessel by means of the arrangements described on page 100. The thermometer sinks immediately, and after the complete solution of the substance the temperature again becomes constant, which is taken as the boiling point of the solution. A known quantity of substance is again added, as the investigations here should not, in general, be limited to a single concentration. The investigations of the same substance should succeed each other without loss of time. At the end of the experiments the quantity of solvent which has been vaporized during the investigations should be determined by repeated weighings of the apparatus.

The accuracy of the results is influenced by the barometric pressure and the temperature of the room.

A difference of 1 mm. in the barometric pressure corresponds, on an average, to a difference of 0.03° in the boiling point.

If the use of the pressure regulator (p. 95) is omitted, care should be taken that no essential variations occur in the barometric pressure while the experiment is being carried out. For unsettled weather a second apparatus, with the pure boiling solvent, can be set up during the experiment. From the readings of the thermometer in the latter apparatus, the necessary corrections for the change of barometric pressure may be easily calculated.

Sometimes it is recommended to work under reduced pressure to prevent decomposition, or under increased pressure to increase the solubility. In this case use may be advantageously made of the simple pressure regulator described on page 95. For this purpose the apparatus of Beckmann (Zeit. phys. Chem. 6, pp. 463 and 464, 1890) should be used.

The influence produced by the temperature of the room is greater, the higher the boiling point of the liquid. Changes in the temperature of the room during an experiment should be avoided.

In order to insure a perfect adjustment of the temperature it is necessary, for boiling-point determinations of pure solvents, to first maintain the boiling from one to two hours before the ther-

mometer is read. The second method of Beckmann, described below, is uninfluenced by the temperature of the room, and therefore specially adapted to solvents of higher boiling points.

Finally, it should be noticed that the recent Beckmann thermometer, graduated to $\frac{1}{50}$ of a degree, and that of F. O. R. Götze, in Leipzig, adapted equally well to freezing points and boiling points, experience a slight change in the value of the degree, owing to the separation of large quantities of mercury. The degrees are smaller for high temperatures, thereby diminishing the elevation of the boiling point and increasing the molecular weight. The error at most for benzene amounts to 1.3 per cent.*

2. METHOD II OF BECKMANN.†

Apparatus and Method of Operation (Fig. 49).—The boiling-vessel *A* consists of a rather long tube about 2.5 cm. in width, in the side tube of which is fastened a coiled condensing tube K_1, and through the upper stopper of which is introduced a Beckmann thermometer.

A platinum wire is fused in the bottom of the tube *A*, which is then filled with glass pearls to a height of 3 to 4 cm.

This boiling-vessel, as shown in the figure, is placed in a vapor jacket *B*, which is made of glass or, for high boiling points, of copper. The jacket is provided with a side tube in which the reflux condenser K_2 is fastened.

The boiling-vessel *A* is fastened in the vapor jacket by means of a cylinder of asbestos *a*, while the space above, between the tube and the jacket, is filled with asbestos wool.

The boiling-tube and the vapor jacket contain the same solvent. The results are thereby made independent of the temperature of the outer room. A small piece of clay may be introduced into the vapor jacket to lessen the boiling.

The vapor jacket with the boiling-tube rests on a small box *C*

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* Beckmann, Zeit. phys. Chem. 6, p. 443, 1890.

† Beckmann, Zeit. phys. Chem. 8, p. 223, 1891. The Beckmann apparatus is furnished by the firm of F. O. R Götze, in Leipzig.

composed of asbestos board and water glass. A vertical section is represented in the figure.

Where the flames fall upon the hot surface is a sickle-shaped opening, covered with wire gauze and asbestos board; the opening is arched over with the edge *d* of an asbestos covering.

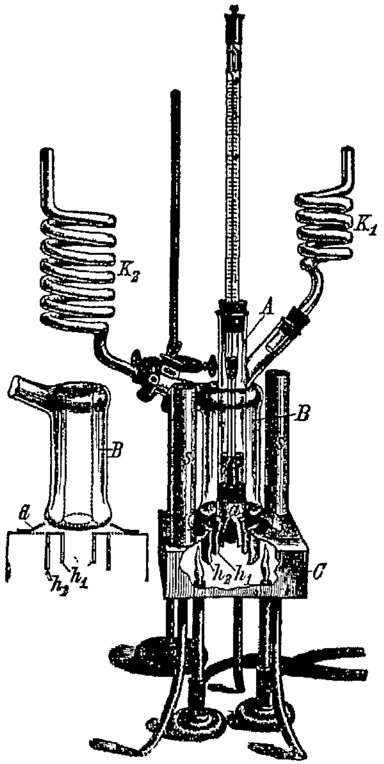

FIG. 49.

The boiling-vessel is protected from the direct action of the flame, from the Bunsen burners placed to the sides, by means of the asbestos rings h_1 and h_2. A small flame under the boiling-vessel is necessary only for water (on account of its high specific heat and heat of vaporization). For all other liquids the boiling of the outer liquid is sufficient to maintain the boiling of the inner liquid.*

The arrangements *s* and *s* serve as outlets for the flame gases.

If the apparatus is to be used for solvents of low boiling points (under 60°), small Liebig condensers may be substituted for K_1 and K_2; for hygroscopic solvents a small calcium chloride tube is attached to the condenser.

The solvent in the inner tube is either weighed in the tube or measured by means of a pipette; the substance (p. 100) is

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* Pařizek and Šule hasten the operation by elevating the temperature of the vapor chamber a few tenths of a degree above the boiling point of the inner liquid, through the addition of a few drops of a substance of higher boiling point.

introduced by means of a pipette or in the form of pastilles. Twenty gm. of solvent is sufficient for the vapor chamber.

A small correction should be applied, owing to the evaporation and condensation in the cooler. According to Beckmann, the quantity of liquid suspended in the vapor chamber amounts to, for very mobile liquids, from 0.15 to 0.2 gm.; for water about 0.35 gm.

For further details of the method see the manipulations given for method I.

APPLICATION OF METHODS I AND II.*

Method I is applicable for solvents with boiling points up to about 130°. In general, the method is preferable for solvents with low boiling points. For solvents with high boiling points (anilin, phenol, etc.) method II is preferable; this method is also preferable for water.

Besides its independence of the temperature of the room, method II has come into special prominence on account of,—

1. The small quantity of the solvent and substance required for the experiment;

2. The more rapid attainment of a constant boiling temperature (thirty to sixty minutes);

3. The more convenient method for heating. A gas pressure regulator is unnecessary.

In reason 1, however, there is also a slight disadvantage, inasmuch as the accuracy is always influenced by the quantity of solvent.

Choice of Concentration and Solvent (for the boiling-point method).—The investigation is begun with a concentration which produces an elevation of about 0.1 or 0.2° in the boiling point, and the content of the solution is gradually increased to ten or twenty per cent. The relations between the percentage content and the calculated molecular weights are represented graphically, and then, in most cases, definite conclusions are drawn regarding the magnitude of the molecular weight.

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* [A more recent form of apparatus has been described by Orndorff and Cameron, Amer. Chem. Jour. 17, p. 507, 1895.—TR.]

The choice of the solvent should always be carefully considered, the choice depending largely on the solubility of the substance and also its boiling point; in general, only such substances are investigated* whose boiling point is at least 130 to 140° above that of the solvent.

If, for the use of a definite solvent, there is any uncertainty in regard to the dissociation of the complex molecules, the substance should be investigated with several solvents.

Substances, especially hydroxyl compounds, dissolved in benzene, chloroform, and carbon disulphide, have a tendency to form complex molecules, which decompose more and more with increasing dilution.

The molecular weights obtained with such solvents as acetic acid, formic acid, thymol, phenol, ether, alcohol, ethyl-acetate, and acetone at higher concentrations are more normal.

In general, ethyl-ether is best adapted to this work. Its low price, its high dissolving capacity, its chemical indifference, and the ease with which the dissolved substance can be obtained again, give it preference over other solvents; also, the volatility and dissociative power are very advantageous for the convenience and accuracy of the determination; in like manner, the large molecular elevation is of special importance. Water is less suitable for the purpose. The number obtained for electrolytes should be carefully tested; the low solubility of non-electrolytes is objectionable. The high boiling point and the small molecular elevation are also a disadvantage.

On the influence of concentration and solvent, see the work of Beckmann, Zeit. phys. Chem. 4, p. 532, 1889; 5, p. 76, 1890; 6, p. 437, 1890; 8, p. 223, 1891.

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* Nernst, Zeit. phys. Chem. 8, p. 128, 1891; also 11, p. 1, 1893. Nernst shows that the boiling apparatus may be used for determining molecular weights of very volatile substances.

CALCULATION OF MOLECULAR WEIGHTS.

According to van 't Hoff,* the following formula holds good:

$$\frac{M(T_1 - T_0)}{p} = \frac{0.02\,T_0^2}{W}.$$

M represents the molecular weight of the dissolved substance; p the number of grams of dissolved substances in 100 gm. of solvent; T_1 and T_0 are the absolute boiling points of the solution and solvent = the observed — 273.2°. $T_1 - T_0$ is therefore the elevation of the boiling point; W is the heat of vaporization of the solvent.

The constant $\frac{0.02\,T_0^2}{W}$ (the molecular elevation of the boiling point) may be determined from the known molecular weight of the dissolved substance, or calculated from the heat of vaporization and the boiling point of the solvent.

The following table (according to Beckmann) † contains the values of this constant for a number of solvents:

SOLVENT.	BOILING POINT.	MOLECULAR ELEVATION OF THE BOILING POINT
Ethyl-ether,	34.97	21.1
Carbon disulphide,	46.2	23.7
Acetone,	56.3	16.7
Chloroform,	61.2	36.6
Ethyl-acetate,	74.6	26.1
Ethyl-alcohol,	78.3	11.5
Benzene,	80.3	26.7
Water,	100.	5.2
Acetic acid,	118.1	25.3
Ethylene-bromide,	131.6	63.2
Phenol,	182.3	30.4
Anilin,	183.7	32.2 ‡

If a solvent is to be used, the constant of which is unknown, the same may be determined by dissolving in the solvent a sub-

* Beckmann, Zeit. phys. Chem. 4, p. 533, 1889.

† According to Pařížek and Šule (Ber. d. d. chem. Ges. 26, p. 1410, 1893) this constant for methyl-alcohol = 9.20, and for iso-propyl-alcohol = 12.9.

‡ In regard to the change of these constants with the boiling point of the solvent for diminished pressure, see Beckmann, Zeit. phys. Chem. 6, p. 463, 1889.

stance of known molecular weight (ligroin, petroleum, ether, aqueous alcohol, etc.).

APPLICATION OF THE BOILING-POINT AND FREEZING-POINT METHODS.

In general, the chemical nature of the substance to be investigated, especially its solubility and volatility, determines which of the two methods is preferable.

The freezing-point method, it is true, is no more convenient to operate than the boiling-point method; but it requires less time, and is also (not considering the investigation of concentrated solutions) capable of greater accuracy. The constants of the molecular depression of the freezing point are greater than the corresponding constants of the molecular elevation of the boiling point. The freezing-point method is preferable for substances which have a tendency to decompose at high temperatures, although the boiling point can be lowered by the use of a pressure-regulator.

The freezing-point method is independent of the barometric pressure, and may be used for the investigation of volatile substances, while the simple boiling-point method has hitherto been limited to substances whose boiling points were at least 130° above that of the solvent (p. 106).

On the other hand, the boiling-point method admits of a larger number of excellent solvents, as ether, alcohol, carbon disulphide, etc. An important advantage is the greater solubility of substances at higher temperatures, and the greater tendency toward the decomposition of the complex molecular groups. For the investigation of concentrated solutions the temperature-reading is more accurate, for no essential change of concentration occurs, as in the freezing method.

XII. SPECIFIC HEAT.

General.—The unit of heat is the calorie.

The calorie is that quantity of heat required to raise the temperature of 1 gm. of water from 0 to 1° (gram-calorie).

If 1 gm. of water is heated to 1° above the temperature of the room, the quantity of heat required is not equal to 1 calorie, but probably somewhat less (a fraction of a per cent.).

Inasmuch as the specific heat of water depends upon the temperature, and as experiments on heat capacity are frequently made at the temperature of the room $t°$ (usually 18°), the calorie at $t°$ (18°) is selected as the unit, so far as the method of mixtures (p. 110) is concerned. It is the quantity of heat required to raise the temperature of 1 gm. of water at $t°$ (18°) 1°.

For the method of melting ice (p. 121) the mean calorie—*i. e.*, the hundredth part of the heat required to raise the temperature of water at 0° to 100°—is usually taken as the unit.

The mean calorie and the calorie at 18° differ, at most, not more than one per cent. The exact relation, at present, is not known with sufficient certainty.

In regard to the large calories for thermo-chemical measurements, see page 132.

The specific heat of a body is the quantity of heat, measured in calories, required to raise the temperature of the unit-mass = 1 gm. of the substance 1°. As the specific heat in general varies somewhat with the temperature, the temperature at which the specific heat is determined should always be specified.

By the method of mixtures, and also the method of melting ice, only the mean specific heat is obtained—*i. e.*, the mean value of the quantity of heat required to raise 1 gm. of the substance 1° in temperature for a given temperature interval $t - t_1$.

If Q is the quantity of heat necessary to raise the temperature of 1 gm. of substance from t_1 to $t°$, then $\frac{Q}{t - t_1}$ is the average specific heat for that temperature-interval.

The mean specific heat increases, in most cases, proportionally

with the temperature, and can be represented by the equation $C_{t-t_1} = a + b\,(t + t_1)$; a and b are constants which can be calculated from two determinations of the mean specific heat for different temperature-intervals. Then the quantity of heat supplied from 0 to $t°$ is $Q_t = a\,t + b\,t^2$, from which it follows that $\frac{d\,Q}{d\,t}$ —*i. e.*, the true specific heat at $t°$ is $K_t = a + 2\,b\,t$.

Usually, a determination of the average specific heat is sufficient.

The product of the specific heat and the atomic or molecular weight is called the atomic or molecular heat.

1. THE METHOD OF MIXTURES.

Principle and Calculation.—A liquid or solid heated to a definite temperature is intimately mixed with a liquid of known specific gravity at a lower temperature. Mixtures involving chemical action must always be excluded. Then the quantity of heat given up by the first body in cooling is placed equal to that taken up by the liquid in the calorimeter on heating, as the heat given out by the system through radiation and conduction is inappreciable.

If P represents the weight (in grams) of the liquid or solid heated to the temperature T, C the unknown specific heat of the same, p the weight of the liquid in the calorimeter at the lower temperature t and of unknown specific heat c, and τ the final temperature assumed by the mixture, then the quantity of heat given up by the heated body is $P\ C\ (T - \tau)$, and the quantity taken up by the liquid in the calorimeter is $p\,c\ (\tau - t)$. Therefore $P\ C\ (T - \tau) = p\,c\ (\tau - t)$.

Inasmuch as the parts of the calorimeter (vessel, stirrer, thermometer) take up a portion of the heat, a correction must be applied to the above equation.

The quantity of heat $c\ (\tau - t)$ must be multiplied by $p + w$ instead of p, where w represents the heat capacity of all the parts of the calorimeter. It is the number of grams of water which corresponds in thermal value to the parts of the apparatus—*i. e.*, the quantity of heat required to raise the temperature of the apparatus 1°. If γ represents the specific heat of the metallic portion of the apparatus, the weight of which is π gm., then the product $\pi\ \gamma$

is the water-equivalent and $\pi \gamma (\tau - t)$ the quantity of heat necessary to raise the temperature from t to $\tau°$. The specific heat of the substance, therefore, is,—

$$C = \frac{(p + w) c (\tau - t)}{P(T - \tau)};$$

or if, as is usually the case, water is employed in the calorimeter, then

$$C = \frac{(p + w)(\tau - t)}{P(T - \tau)},$$

since c may be placed approximately equal to unity (p. 109).

(*a*) Specific Heat of Solids.

Heating Vessel.—A vessel of the form of figure 50 may be employed. The substance is heated by means of the vapor of

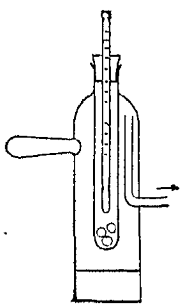

Fig. 50.

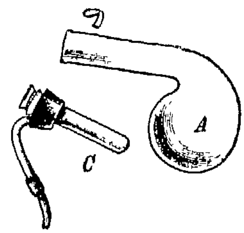

Fig 51

boiling water (and other liquids) until the temperature of the thermometer is constant. If no thermometer is at hand, the boiling temperature is calculated from the barometric pressure.*

Very advantageous also is the short-necked retort A (Fig. 51) composed of copper or glass, in which water, nitrobenzene, diphenylamine, etc., may be kept vigorously boiling.

Not too small a quantity of the substance is placed in the small tube C. The heating of the retort is so adjusted that the vapor of the liquid condenses, for most part, at D. At a given moment the

* Landolt-Börnstein, Physik. Chem. Tab., pp. 48 and 49, 1883.

substance in the calorimeter is introduced into the retort, so that none of the heating liquid flows out.

The substance, especially if it is a poor conductor of heat, is used in small pieces and weighed in the tube. As a portion of the substance frequently clings to the tube, the tube is reweighed after the experiment.

Pulverized substances or small granules, as well as substances which act chemically on the liquid in the calorimeter, are enclosed in a small metallic vessel made of platinum gauze, or in a platinum shell soldered with gold. The weight of the platinum, multiplied by the specific heat = 0.0324, is the water-equivalent of the small vessel.

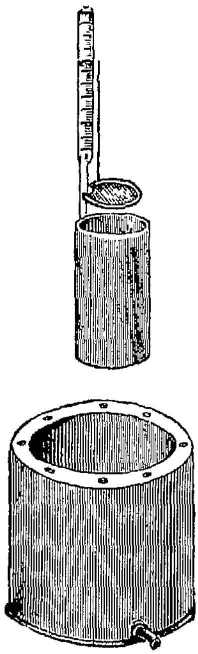

FIG. 52.

The Calorimeter (Fig. 52).—The calorimeter consists of a cylindrical, thin-walled vessel, made of platinum, silver, or brass. Glass vessels * are used only for very rough determinations.

The outer surface of the vessel is polished to prevent radiation. The length of the cylinder is somewhat greater than the diameter; the capacity should be at least 200 c.c., and, better, 500 c.c.

To prevent a considerable loss of heat to surrounding bodies, the calorimeter, resting on three pieces of cork, is placed in a larger double-walled brass vessel. The space between the walls is filled with water, and the size of the vessels so adjusted that the distance between the inner and outer vessel is about 5 cm. at all points.

During the investigation the vessel is provided with a cover. For accurate determinations the inner calorimeter vessel, resting on pieces of cork, is placed in one or two larger brass vessels, and these in turn placed in the outer double-walled vessel.

* Nernst, Zeit. phys. Chem. 2, p. 24, 1888; Bersch, Zeit. phys Chem. 8, p. 388, 1891; and Kohlrausch, Prakt. Phys. VII, p. 119, 1892.

The calorimeter is provided further with a small, suitable stirrer (platinum, brass, etc.) and a carefully tested thermometer (see under 3, chap. xx).

The stirrer may have the form represented in figure 52. A metallic wire, movable in a vertical direction, is soldered to a metallic gauze, which is provided with a slit for the thermometer; or a metal ring is soldered to a metallic wire at an angle of 90°. The stirrer may also have the form of a screw (Fig. 58, p. 131).

The thermometer, for accurate observations, is graduated to $\frac{1}{50}$ or $\frac{1}{100}$ of a degree, and is read by means of a microscope accurately to $\frac{1}{500}$ of a degree.

The heating vessel and calorimeter should be separated by means of a cardboard screen.

Method of Operation.—When the substance has been heated to the desired temperature, and the temperature of the water in the calorimeter has been accurately determined, the substance is allowed to fall into the calorimeter with the necessary precaution, and, during constant stirring, the maximum temperature τ is read off.

The stirring must be carefully done. In using the stirrer represented in figure 52, care should be taken not to remove any portion of the substance above the liquid.

If water can not be employed, use may be made of such liquids as turpentine (sp. H. = 0.43), toluene (sp. H. = 0.40), and anilin (sp. H. = 0.49).

The corrections to be applied are: (1) That for the water-equivalent of the calorimeter, stirrer, and thermometer; (2) for the loss of heat by radiation.

The water-equivalent of the metallic portions is obtained by weighing the calorimeter vessel, together with the stirrer. Only the portion of the stirrer, however, which is immersed in the liquid is to be taken into account. Let the combined weights $= \pi$ and the specific heat of the metal $= \gamma$, then $\pi\gamma$ is the water-equivalent (γ for platinum $= 0.032$, for silver $= 0.057$, and for brass, with sufficient accuracy $= 0.094$). If the combined weights are not more than 20 gm., the water-equivalent $\pi\gamma$ for platinum is only 0.64, and for brass 1.88 gm.

The water-equivalent of the portion of the thermometer immersed in the liquid is determined most simply by estimating the

volume of the same by sinking into a graduated vessel. Inasmuch as 1 c.c. of glass has the same water-equivalent, $2.5 \times 0.19 = 0.47$, as 1 c.c. of mercury $= 13.6 \times 0.034 = 0.46$, it is only necessary to multiply the volume v in cubic centimeters, of the portion of the thermometer immersed, by 0.46 to obtain the water-equivalent.

The total water-equivalent of the apparatus, then, is $w = \pi \gamma + 0.46\, v$.

The water-equivalent of the thermometer may be determined somewhat more accurately by heating the same in a flame or in a mercury bath to 40–50° and then immersing it in the water in a calorimeter. If m is the weight of the water in grams, $t_2 - t_1$ the increase of temperature, and $t_3 - t_2$ the decrease in the temperature of the thermometer, then,—

$$m\left(\frac{t_2 - t_1}{t_3 - t_2}\right)$$

is the water-equivalent of the thermometer.

The loss of heat through radiation is easily understood, for it is evident that, when the calorimeter is heated above the temperature of the surroundings, a continual loss of heat takes place, which increases with the difference in the temperatures of the calorimeter and the surroundings The final temperature, then, is too small by an amount Δ.

The influence of the radiation can be neglected as inappreciable only when the adjustment of the temperature takes place quickly, and the maximum temperature is not more than 2–3° above that of the surroundings. It is also necessary that the capacity of the calorimeter should be at least 500 c.c. The larger the calorimeter, the less the influence of radiation.

Before the investigation is begun, the calorimeter, etc., should be left in the observation room for some time, until the calorimeter, the water content of the surrounding jacket, and the liquid to be employed have assumed the temperature of the room.

The method of Rumford, in which the initial temperature of the calorimeter is adjusted (from a previous experiment) so as to be as much below the temperature of the surroundings as the final temperature is above, can lead, in some measure, to accurate results only when the temperature adjustment takes place quickly

and the temperature change amounts to not more than 4 to 5°. To prevent the condensation of moisture on the outer wall of the colorimeter, the same should be cooled, before the experiment, to at least 2° below the temperature of the room.

If the investigation requires considerable time, or if there is a considerable increase or decrease in temperature, then the influence of the radiation must be fully taken into account. For determining this correction, the method of Regnault-Pfaundler * is, perhaps, most free from objection.

1. **The Fore-period.**—Before the investigation is begun, the temperature of the calorimeter is observed at equal intervals of time, from minute to minute, for a period of ten minutes.

Let these temperatures be $\vartheta_0\ \vartheta_1\ \vartheta_2\ \vartheta_3\ \vartheta_4\ \ldots\ \vartheta_{10}$. If the experiment is begun at the moment when ϑ_{10} must be read off, then ϑ_{10} can not be determined directly, but it is:

$$\vartheta_{10} = \vartheta_9 + \frac{\vartheta_0 - \vartheta_9}{9};$$

$\frac{\vartheta_0 - \vartheta_9}{9}$ is the average temperature change per minute for the first nine minutes of the fore-period.

2. **The Principal Period.**—The principal period begins at the moment when the experiment is begun. An increase of temperature follows, which is observed to a maximum temperature; after which the temperature decreases, on account of the radiation. The decrease at first is not uniform, as would be the case if the substance had given up all its excess of heat to the calorimeter immediately after reading off the maximum temperature.

It is assumed that the principal period continues through ten minutes—*i. e.*, after ten minutes the decrease of temperature from minute to minute is uniform.

Then $\vartheta_{10} = t_0$ is the temperature at the beginning of the investigation, and $t_1\ t_2\ t_3\ t_4\ \ldots\ t_{10}$ the temperatures observed from minute to minute during the principal period.

3. **The After-period.**—Finally, $t_{10} = \tau_0$, and $\tau_1\ \tau_2\ \tau_3\ \tau_4\ \ldots\ \tau_{10}$ are the temperatures observed from minute to minute during the after-period—*i. e.*, the period in which the temperature change, due

* Other corrections, Berthelot, Méc. chim. 1, p 208, 1879; Wiedemann and Ebert, Phys. Prakt., pp. 187 and 215, 1890.

to radiation, has become uniform. Let the temperature changes during the fore-, principal, and after-periods be represented by Δ^ϑ, Δ^t, Δ^τ, then the mean temperature changes of the fore- and after-periods correspond to the mean temperatures ϑ_5 and τ_5 of the two periods; that is,—

$$\Delta_5^\vartheta = \frac{\vartheta_0 - \vartheta_{10}}{10} \text{ and } \Delta_5^\tau = \frac{\tau_0 - \tau_{10}}{10}.$$

It can be assumed, then, that the differences in the temperature changes Δ stand in the same ratio as the differences in the corresponding temperatures; if, therefore, t_n and Δ_n^t represent any given values for the principal period, we have the following proportion:

$$(\Delta_n^t - \Delta_5^\vartheta) : (\Delta_5^\tau - \Delta_5^\vartheta) = (t_n - \vartheta_5) : (\tau_5 - \vartheta_5);$$

or,

$$\Delta_n^t = (t_n - \vartheta_5) \frac{\Delta_5^\tau - \Delta_5^\vartheta}{\tau_5 - \vartheta_5} + \Delta_5^\vartheta.$$

If for t_n is substituted the mean value of the temperature read off at the beginning and end of the nth minute, and for n all values from $n = 0$ to $n = 10$, the loss by radiation for each of the ten minutes of the principal period is obtained. If the sum of these Δ's is added to the final temperature t_{10}, we obtain $t_{10} + \Sigma\Delta$ as the corrected final temperature free from the influence of radiation.

It is calculated in the following manner:

$$\Sigma\Delta = (\Delta_1^t + \Delta_2^t + \Delta_3^t + \ . \ . \ . \ \Delta_{10}^t)$$
$$= \left(t_1 + t_2 + \ . \ . \ t_9 + \frac{t_0 + t_{10}}{2} - 10\,\vartheta_5\right) \frac{\Delta_5^\tau - \Delta_5^\vartheta}{\tau_5 - \vartheta_5} + 10\,\Delta_5^\vartheta.$$

The following example* will serve to illustrate the method.

The temperature of the room is 23.5, and the temperature of the calorimeter is read off every twenty seconds. The observed temperatures of the calorimeter are as follows:

TIME.	TEMPERATURE.	TIME.	TEMPERATURE
0.20″	19.78°	9.20″	24.22°
1.20″	19.80°	10.20″	24.22°
2.20″	19.82°	11.20″	24.22°
3.20″	19.84°	12.20″	24.215°
4.20″	(Beginning of Experiment.)	13.20″	24.215°
5.20″	23.54°	14.20″	24.210°
6.20″	24.10°	15.20″	24.207°
7.20″	24 19°	16.20″	24.204°
8.20″	24.21°	17.20″	24.200°

* Wüllner, Physik. 3, p. 407, 1875.

From the 14th interval the temperature decreases uniformly, 0.01° in 3.20″. The value 0.003° corresponds here to Δ_5^τ in the formula, and the temperature 24.205° corresponds to the value τ_5.

In the fore-period the temperature increases by 0.02° each interval. The temperature immediately before the experiment, therefore, is 19.86°; the temperature 19.82° corresponds to the value ϑ_5, and — 0.02° corresponds to Δ_5^ϑ. The negative sign must be taken into consideration. If the calorimeter before the investigation, as in this case, is at a lower temperature than that of the surroundings, the value is negative, otherwise positive. Hence:

$$\Sigma\Delta = \left(23.54 + 24.10 + 24.19 + 24.21 + 24.22 + 24.22 + 24.22 + 24.215 + 24.215 + \frac{19.86 + 24.21}{2} - 10 \times 19.82\right) \left(\frac{0.003 + 0.02}{24.205 - 19.82}\right) - 10 \times 0.02;$$

or,

$$\Sigma\Delta = 0.015,$$

and the corrected temperature,—

$$= 24.210° + 0.015 = 24.225°.$$

(b) Specific Heat of Liquids.

Method of Kopp and Schiff.—The specific heat of a liquid may be determined in the manner already described, except that the liquid must be enclosed in a suitable vessel, which, after heating, is immersed in the water of the calorimeter. The form and size of the calorimeter, as well as the stirrer, should conform, as far as possible, with the heating vessel. A ring-shaped stirrer is best adapted to this work. If w_1 is the water equivalent of the heating vessel, the calculation may be made from the following formula:

$$(P\,C + w_1)\ (T - \tau) = (p + w)\ (\tau - t),$$

in which w has the same meaning as on page 110.

According to the method of Kopp, small, thin-walled, glass vessels, about 6 cm. high and 1.5 cm. wide, and provided with a narrow neck about 10 cm. in length, are used as the heating vessels. The filling is accomplished by means of the arrangement

described on page 30 (Fig. 11). The vessel is heated in a mercury bath. The mercury during constant stirring is heated uniformly on a water-bath or, better, in an oil-bath, which, in turn, is placed in a sand-bath covered with cotton. Simple beaker glasses may be used to contain the mercury and oil. The wide portion of the heating vessel is completely immersed in the mercury, and the thermometer, which has been previously adjusted, is placed in the immediate vicinity of the vessel By regulating the flame, the temperature of the bath may be kept constant to within 0.1 to 0.2 of a degree.

The water-equivalent w_1 of the heating vessel of the weight π gm. is approximately equal to $0.19\ \pi$.

The method leads to more accurate results if the calorimeter and heating vessel are of the form proposed by R. Schiff.*

The inner vessel of the calorimeter, which is best constructed of platinum, has a capacity of about 600 gm., and contains 500 gm. of water. The total water-equivalent (including thermometer) may amount to about 5 gm. (sp. H. of platinum $= 0.0324$).

A platinum vessel of the form represented in figure 53 with the cross-shaped outline may be used as a heating vessel. Its capacity is about 70 c.c., the inner width of an arm is about 1 cm., and the water-equivalent about 4 gm.; the vessel is filled to five-sixths of its capacity with water. Of special advantage is its large, good-conducting, cooling surface; for an elevation of 5° in the temperature of the calorimeter, the maximum temperature is attained in from one and one-half to two minutes. Another advantage lies in the fact that the vessel itself serves as stirrer.

The vessel is heated in the vapor of a suitable liquid (acetone, methyl-alcohol, benzene, water, toluene, xylene, and mixtures) in the apparatus represented in figure 54.

A funnel-shaped copper vessel is heated in the vapor of a boiling liquid in the heating flask, and is connected above with a reflux condenser by means of two symmetrical tubes joined together in the form of a Y. In the upper portion of the vessel is soldered a cross-shaped copper shell, about 10–12 cm. in length, and closed at the lower end; the platinum vessel of corresponding shape can

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*R. Schiff, Ann Chem. Pharm. 234, p. 302, 1886.

be easily introduced into this shell. The vessel, after heating with a spirit-lamp, is provided with a thermometer, placed in a copper shell, covered with a perforated copper plate, which in turn is covered with flannel, and heated for about twenty to thirty minutes, until the temperature has become constant for some time, and then quickly introduced into the calorimeter, which is protected by means of a wood or cardboard screen.

The thermometer is removed, however, before introducing into

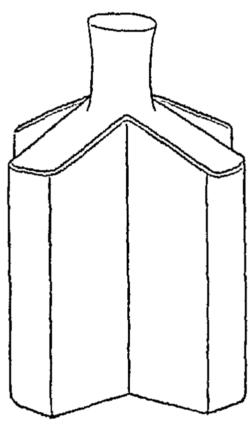

FIG. 53

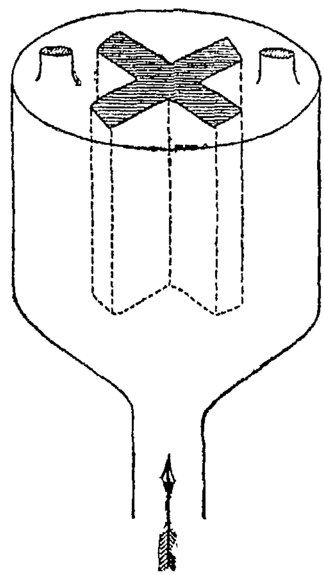

FIG. 54.

the calorimeter, and can be replaced by a small calcium chloride tube. In order to remove the thermometer easily, and have a convenient handle for introducing the vessel into the calorimeter, a thin-walled glass tube, as wide as possible and about 6–8 cm. in length, is fastened in the neck of the vessel by means of a cork ring, so that the tube does not project below the cork into the vessel. The thermometer is then loosely placed in, and when it is read, the projecting thread must be taken into consideration.

The observation error of the method influences the result only from 0.5 to, at most, 1 per cent.

Method of Andrews.—When somewhat larger quantities of a liquid are at hand, this method may be advantageously used.

A heating substance, heated to a definite temperature, is immersed (1) in the liquid to be investigated, (2) in water; then, as the substance gives up equal quantities of heat to the two liquids, we have the following equation:

$$(P\,C + w)\,(T - t) = (P_1 + w)\,(T_1 - t_1),$$

in which P, C, and $T - t$ represent the weight, specific heat, and temperature elevation of the liquid, P_1, $T_1 - t_1$ the weight and temperature elevation of the water, and w the water-equivalent of the calorimeter (pp. 110 and 113).

The heating substance consists of a thin-walled glass globe of 5 to 10 c.c. capacity filled with mercury. Onto the globe is fused a capillary tube (50 cm. in length and from 0.6 to 1 mm. in diameter) provided with two marks and supplied with a funnel at the top. The distance between the marks is such that the mercury thread reaches the two marks when heated to about 30 and 80°. In regard to the filling of the glass globe, and its heating in a mercury bath, see pages 77 and 118. The globe is introduced into the calorimeter at the moment when the cooling mercury passes the upper mark, and as soon (with constant stirring) as the lower mark is reached the vessel is removed from the calorimeter, the temperature of which is then read off.

Tables of specific heats, see Berthelot, Méc. chim. I, pp. 434, 456, 467, and 495, 1879; Thomsen, Therm. Unters. I, p. 46, 1882; Landolt-Börnstein, Tabellen, pp. 174 to 186, 1883. Specific heats of organic compounds, R. Schiff, Lieb. Ann. 234, p. 300, 1886. Specific heats of gases, Wüllner, Exper. Physik. III, p. 423, 1875; E Wiedemann, Pogg. Ann. 157, p. 1, 1876, and Wied. Ann. 2, p. 195, 1877.

DETERMINATION OF SPECIFIC HEAT WITH THE ICE-CALORIMETER.

METHOD OF BUNSEN.

Apparatus and Method in General.—A heated substance is introduced into the calorimeter (Fig. 55) where a definite quantity of ice is melted. The quantity of ice melted is calculated from the change of volume, and from this the quantity of heat given up by the substance can be calculated.

The calorimeter, which is made of glass, consists of an inner tube fused to an outer cylindrical or oval glass mantle *V*.

This glass mantle is narrowed at the bottom into a smaller tube, which is bent upward and provided, at the upper end, with a small funnel, and connected, by means of a forking arrangement, with the capillary tube *S*.

The wider portion of the glass mantle *V* is filled with water and the lower part with mercury. The mercury also completely fills the tube *S*, the outlet of which is immersed in a small vessel filled with mercury.

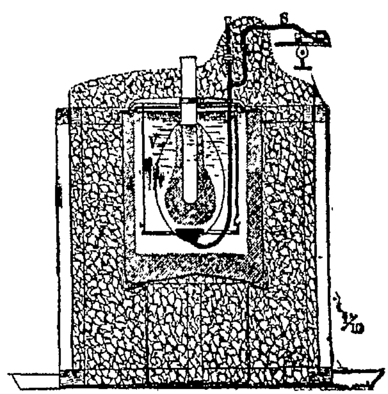

FIG. 55

The water in *V* is in part brought to freezing, and the apparatus *i* and *J* filled with ice and ice-water, so that the whole system assumes the temperature 0°. The introduction then of a heated substance into the inner tube will convert a definite quantity of ice at 0° to water at 0°. This melting process is accompanied by a decrease in volume, which is evident from the fact that the capillary-tube sucks in a definite quantity of mercury from the small vessel.

Calculation.—If this quantity of mercury, obtained by weighings of the mercury basin, is a gm., then the corresponding volume at 0° is

$$= \frac{a}{13.596} \text{ c.c.}$$

This represents the decrease in volume due to the melting of the ice. According to Bunsen, 1 gm. of ice at 0° has the volume of 1.09082 c.c., and 1 gm. of water at 0° the volume of 1.00012 c.c. The melting, therefore, of 1 gm. of ice produces a decrease of 0.0907 c.c. in the volume.

As the volume has been decreased by

$$\frac{a}{13.596} \text{ c.c.},$$

the quantity of ice melted is

$$\frac{a}{13.596 \times 0.0907} \text{ gm.}$$

The melting of one gm. of ice requires 79.9 calories (heat of fusion).

The melting of

$$\frac{a}{13.596 \times 0.0907} \text{ gm.}$$

of ice is equivalent, therefore, to

$$\frac{a\ 79.9}{13.596 \times 0.0907} = \frac{a}{0.01544} \text{ mean calories (p. 109) of heat.}$$

This quantity of heat has been added to the calorimeter by the heated substance. If the quantity of substance $= p$ gm., its temperature in Celsius degrees $= t$, then the mean specific heat of the substance between 0 and $t°$ is

$$\frac{a}{0.01544\,p\,t}.*$$

Apparatus and Method in Detail.—The filling of the glass mantle V with previously boiled water and mercury may be accomplished in the following manner:

The upper end of the tube, which extends from the bottom of the apparatus, is immersed in recently boiled water, whence the glass mantle, by careful heating, is filled to about one-third of its length with water. The liquid which has been sucked in is heated to boiling, and the open end of the tube immersed in boiling

* The quantity of mercury corresponding to a mean calorie can be determined directly by introducing known quantities of water at $t°$ in small glass bulbs into the calorimeter. (Schuller and Wartha, Wied. Ann. 2, p. 359, 1877.)

water. When the water in the glass mantle is for the most part evaporated, the liquid is allowed to rise again, and the vessel is in that way completely filled with water free from air. Previously boiled mercury is then poured in until it has the same height in the two limbs of the tube (see the wider tube in figure). The water in the narrower tube is then removed by means of a pipette, the walls are dried, and it is then filled with mercury by means of a capillary-tube, so that no air-bubbles adhere to the sides.

The funnel and the capillary suction-tube *S* must be fastened in the mantle-tube mercury-tight.* The latter is a bent tube (Fig. 56), which widens into a pear-shaped opening at the end which is immersed in the small basin. This widening is necessary to maintain a perfect contact between the inner and outer mercury, which might otherwise be disturbed by the influence of capillarity.

The tube may be prepared in the following manner: The tube is filled with colored liquid and fused together at one end, which is then ground off with glycerine and a fine oil-stone, until the opening is about 0.5 mm. in diameter.

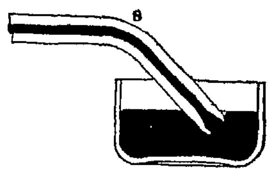

FIG. 56.

The well-cleansed suction-tube is fastened to the glass mantle, when the ice-formation in the same has taken place.

A beautiful cylinder of ice can be produced in *V* (see the shading in the figure) in the following manner:

Two flasks from one-half to one liter capacity, one of which contains a large quantity of alcohol, are surrounded by a freezing mixture (salt and snow) at about — 15° to — 20°. The flasks are then connected, by means of doubly perforated corks, with the inner tube of the calorimeter, so that the strongly cooled alcohol, by means of a pump, can be sucked through the tube a number of times, changing from one flask to the other. The calorimeter is placed at the same time in snow or ice-water (better, not in freezing mixture).

There is formed then, after two to three hours, from the interior

* The funnel is not necessary. The tube may be closed with a stopper; the apparatus is then less liable to be broken.

outward, a clear ice-mantle, which may easily be obtained from 5–10 mm. in thickness, and which will suffice for a large number of investigations. The ice-mantle should not adhere too tightly to the inner wall. The ice, therefore, in immediate contact is thawed by repeatedly filling the tube with water some degrees above 0°.

After obtaining the ice-mantle, the apparatus is packed. If perfectly clean, freshly fallen snow is at hand (kept in a clean box), the calorimeter is packed as completely as possible in a larger vessel, which is provided with an outflow-cock for the molten ice.

When snow is lacking, use is made of the arrangement represented in the figure.

The two vessels *J* and *i* are made of zinc-plate. An ice-mantle is formed in the inner vessel from pure distilled water. This mantle surrounds the walls of the vessel to a thickness of 2 to 3 cm. The surface of the water in *J* is covered with a finely pulverized ice, and the vessel then provided with a well-closed metallic cover. The outer vessel is filled with pieces of ordinary ice, provision being made for the water which is formed to escape.

If the apparatus is so packed and placed in an ice-chest or a specially cold room, a large number of determinations can be carried out at long intervals without difficulty.

If the snow or ice-water in the vessel *J* is not perfectly pure, the thickness of the ice-mantle in *V* changes continually. The accompanying volume change will influence the results more or less.

For the use of pure snow and ice-water a continual decrease in the melting of the ice-cylinder in *V* takes place. This is stirred, therefore; for, on account of the mercury pressure, the melting temperature in *V* is a little below 0°, and hence a continually less supply of heat from without takes place.

The investigation is made by connecting the calorimeter with a suitable pressure apparatus, extension of the suction-tube from below, or by occasioning an increase or decrease in the ice-cylinder through the introduction of traces of common salt into the vessel *J*.

The thawing of the ice-mantle can usually be regulated by raising or lowering the point of the suction-tube in the mercury basin, so that the amount of mercury in the basin decreases only a few milli-

grams per hour. This change of weight for the period of the investigation—usually twenty to thirty minutes—must be taken into account. Two mercury basins are necessary, which, changing every half hour, are weighed and connected with the calorimeter (gently tapping the suction-tube). If the thawing of the ice-mantle in equal intervals of time is uniform, the investigation may be commenced. The small corrections are then calculated from weighings before and after the time of the investigation.

The investigations are carried out in a room the temperature of which, at most, should not be more than 5 to 10° above 0°.

The inner tube of the calorimeter contains some glass-wool on the bottom, and is partially filled with water (or some other suitable liquid). Its cork is removed only for the introduction of the substance. The latter is heated to a constant temperature in a heating vessel (p. 111). The heating vessel and calorimeter are separated by means of a cardboard screen, and set up so that an easy and quick transfer is possible.

Pulverized solids are introduced in platinum shells (specific heat = 0 0324); liquids are introduced in small glass globes, which are filled, almost completely, at the temperature of the heating vessel, and then fused together. The specific heat of the glass (on an average 0.19) should be determined by a previous investigation, and the water-equivalent (pp. 110 and 113) taken into consideration. Three-tenths to one gm. of substance is sufficient for most determinations.

Ice-calorimeter and Mixture-calorimeter.—The ice-calorimetric method has the advantage over the mixture-calorimeter of a greater and even extraordinary accuracy for the use of small quantities of substances; the substantially lower cost of the apparatus, in comparison with the better mixture-calorimeter, should also be mentioned. On the other hand, extreme care is required in working with the ice-calorimeter.

In regard to the ice-calorimeter, see: Bunsen, Pogg. Ann. 141, p. 1, 1870; * Schuller and Wartha, Wied. Ann. 2, p 359, 1877; Blümcke, *ibid.* 25, p. 154, 1885; Dieterici, *ibid.* 33, p. 425, 1888, and 38, 1889 Literature on the use of the ice-calorimeter for measuring the heats of solution, neutralization, vaporization, and combustion, see the following chapters.

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* This method of measuring the mercury in a graduated tube is less accurate than the modified method of Schuller and Wartha.

XIII. HEAT OF FUSION.

By the heat of fusion is meant that quantity of heat, measured in calories, which is required to melt 1 gm. of a substance.

The heat of solidification is the quantity of heat set free when 1 gm. of a substance is changed to a solid state.

The molecular heat of fusion or solidification is the product of molecular weight and the heat of fusion or solidification, therefore the heat of fusion or solidification referred to one molecular weight in grams.

Principle and Calculation.—The method of mixtures is usually employed.

1. If the melting point of the substance is below the temperature of the room (benzene, etc.), the substance is allowed to solidify and is introduced, in a suitable vessel, into the calorimeter, which contains at least enough liquid, so that the final temperature is above the melting temperature of the substance.

The quantity of heat which the introduced substance takes up is the sum of three values:

(*a*) The quantity of heat taken up in heating from the temperature t_1, the temperature of the solid substance when introduced into the calorimeter, to the melting temperature t_0. A knowledge, therefore, of the specific heat c_1 of the solid is necessary.

(*b*) The quantity of heat taken up in changing from the solid to the liquid state at the temperature t_0 (heat of fusion).

(*c*) The quantity of heat required to heat the liquid from the temperature t_0 to the final temperature of the calorimeter τ. The specific heat c_2 of the liquid substance must therefore be known.

Let L represent the heat of fusion of the substance, p_1 the weight in grams of the substance used, p_2 the weight of the water in the calorimeter, the initial temperature of which is T; w_1 the water-equivalent of the vessel containing the substance, w_2 the water-equivalent of the different parts of the calorimeter; then the quantity of heat given up by the calorimeter and contents

$= (p_2 + w_2)\ (T - \tau)$, and the quantity of heat taken up by the substance and vessel

$$= p_1\,[c_1\,(t_0 - t_1) + L + c_2\,(\tau - t_0)] + w_1\,(\tau - t_1).$$

By equating these two values we obtain

$$L = \frac{(p_2 + w_2)(T - \tau) - w_1\,(\tau - t_1) - p_1\,[c_1\,(t_0 - t_1) + c_2\,(\tau - t_0)]}{p_1}$$

2. If the melting point of the substance is below the temperature of the room in general, the heat of solidification is determined. The procedure is the reverse of that just described.

The substance is heated above the melting point t_0 to the temperature t_1, and introduced into the calorimeter, the temperature τ of which lies below the temperature t_0. Then, if E is the heat of solidification of the substance, and the remaining letters have the meaning given above, the quantity of heat given up by the introduced substance (+ vessel) is

$$= p_1\,[c_2\,(t_1 - t_0) + E + c_1\,(t_0 - \tau)] + w_1\,(t_1 - \tau)$$

and the quantity of heat taken up by the calorimeter

$$= (p_2 + w_2)(\tau - T).$$

Therefore

$$E = \frac{(p_2 + w_2)(\tau - T) - w_1\,(t_1 - \tau) - p_1\,[c_2\,(t_1 - t_0) + c_1\,(t_0 - \tau)]}{p_1}.$$

Method of Operation.—The chapter on Specific Heat may be referred to here. The solid or liquid substance is usually introduced in a small, thin-walled flask (p. 118). The specific heats of the solid and liquid substances are determined for the temperature-interval of the experiment. The influence of radiation is to be taken into consideration, as described on page 115.

The determination of the heat of solidification according to the above method is sometimes very uncertain. Very different values are frequently obtained for the heat of fusion and solidification. This indicates that substances, after solidifying, are not always in the same condition. The determination of the heat of solidification, therefore, is avoided in many cases.

Assuming the substance to be soluble in the liquid in the calor-

imeter, and its melting point to be *e. g.* 60°, then the following values must be determined:

(*a*) The heat of solution of the solid substance at the temperature of the room (18°) according to page 137.

(*b*) The specific heat of the solid for the temperature interval, from the temperature of the room to a little below the melting temperature. This specific heat may be easily calculated if the quantity of heat, apart from the heat of solution of the substance dissolved at the temperature of the room, is known, which is given up by the substance, previously heated to about 55°, when dissolved in the liquid in the calorimeter.

(*c*) The specific heat of the liquid substance for the temperature interval 65°–100°. This value is calculated from the difference between the quantity of heat given up when the liquid substance, heated to 65°, is dissolved in the calorimeter at the temperature of the room, and that given up when the substance at 100° is dissolved at the temperature of the room.

If these three values are known, the heat of fusion may be easily calculated; for the total quantity of heat which 1 gm. of the molten substance heated to 65° gives up in the calorimeter, is the sum of: (*a*) The specific heat of the liquid substance multiplied by the temperature interval 65°–60°; (*b*) the heat of fusion at 60°; (*c*) the specific heat of the solid substance multiplied by the temperature interval 60°–18°; and (*d*) the heat of solution of 1 gm. of the substance at 18°.

CALCULATION OF THE HEAT OF FUSION FROM THE DEPRESSION OF THE FREEZING POINT.

This indirect method can be used only for approximate determinations.

According to van 't Hoff we have:

$$L = \frac{0.02\,T^2}{\Delta}.$$

L represents the heat of fusion of the solvent, T the absolute freezing point of the same, and Δ the molecular depression of the freezing point for the given solvent. The variations between the

observed and calculated values amount to usually less than 5 per cent.

See p. 90 and van 't Hoff, Zeit. phys. Chem 1, p. 497, 1887; Eykmann, *ibid.* 3, p. 208, 1889.

Tables of heats of fusion, Berthelot, Méc. chim. 1, p. 423, 1879, and Landolt-Börnstein, Tabellen, p. 188, 1883.

XIV. HEAT OF VAPORIZATION.

By the heat of vaporization is meant the quantity of heat, measured in calories, which is required to change 1 gm. of a liquid at its boiling point to a vapor at the same temperature. The heat of vaporization is equal to the heat of condensation.

The molecular heat of vaporization is the product of the molecular weight and the heat of vaporization.

METHOD OF R. SCHIFF.

Principle and Calculation.—The heat of condensation is here determined. A definite quantity of liquid is vaporized and the vapor, freed from all previous condensations, is condensed to a liquid in a calorimeter.

If p is the weight in grams of the liquid changed to vapor, T the boiling point, τ the final temperature in the calorimeter, c the mean specific heat of the liquid between T and $\tau°$, and V the heat of vaporization, then the quantity of heat in calories, which the condensed vapor gives up to the calorimeter is, $p\,[c\,(T - \tau) + V]$, and the quantity of heat taken up by the calorimeter and contents, if P is the quantity of water in grams, w the water-equivalent of the parts of the calorimeter and t the initial temperature, is $(P + w)\,(\tau - t)$. By equating these two values we obtain:

$$V = \frac{(P + w)\,(\tau - t) - p\,c\,(T - \tau)}{p}.$$

Apparatus and Method of Operation.—The calorimeter has the usual form (see chapter on Specific Heats). It is made of brass

surrounded by a water mantle, and contains about one liter of water.

The liquid is vaporized in a small round flask, which is placed at some distance from the calorimeter, and is connected by means of a stopper with a wide glass tube, about 30 cm. long, which is bent upward at an angle of 120°. This tube is wrapped with wadding as far as possible, and is surrounded by an outer tube. The vapor passes from the inner tube into the arrangement represented in figure

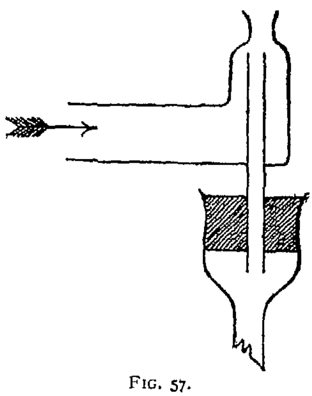

FIG. 57.

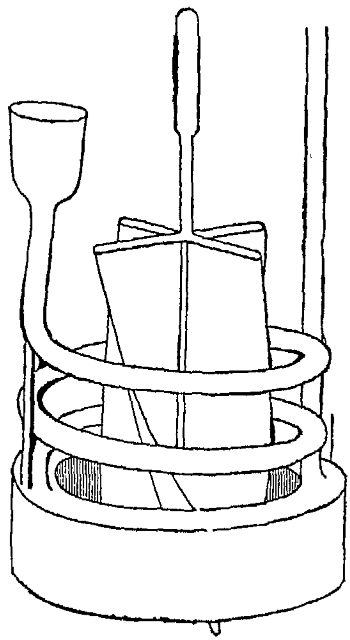

FIG. 58.

57, which is best made of silver. The inflowing vapor moves first in the direction of the arrow, then into the inner silver tube adjusted almost to the upper opening, then downward, when the temperature of the tube will become the same as that of the vapor. A previous condensation is in this way avoided. The vapor then passes into the (silver) coiled tube (Fig. 58) connected by means of a cork. This tube projects at most from 2 to 3 mm. out of the water in the calorimeter. The coiled tube terminates below in a

vessel of about 70 c.c. capacity, in which the condensed liquid is collected.

The thermometer is introduced into the middle of the calorimeter, or between the metallic coil and the wall of the calorimeter, after which a ring-shaped stirrer or the specially adapted stirrer (Fig. 58) of brass with an ivory handle is arranged.

On the determination of the water-equivalent (calorimeter, stirrer, thermometer), see pp. 110 and 113; the same is about 15 to 20 gm.

During the investigation the calorimeter and thermometer are carefully protected from the influence of the radiation at the sides of the heated vessel and the hot conducting tube by means of card-board screens.

For estimating the temperature, the loss of heat by radiation must be taken into account according to p. 115, as the time of the experiment amounts to at least five minutes.

The weight of the liquid vaporized is determined by weighing in the coiled tube. Sufficient liquid (20 to 30 gm.) is vaporized, so that the increase in the temperature of the water in the calorimeter amounts to 4 to 5°.

At the end of the investigation, after removing the flame, the small stopper (Fig. 57) should be loosened, otherwise the rapid rushing in of air may remove a portion of the liquid from the coiled tube. Substance for investigation: water, heat of vaporization = 537.3 calories.

HEAT OF VAPORIZATION AND ELEVATION OF THE BOILING POINT.

The heat of vaporization can be approximately calculated from the elevation of the boiling point, just as the heat of fusion can be calculated from the depression of the freezing point. The formula is as follows:

$$W = \frac{0.02\, T_0^2\, p}{M[T_1 - T_0]}.$$

See p. 107. Tables of heats of vaporization, see Berthelot, Méc. chim. 1, p. 418, 1879, and Landolt-Börnstein, Tabellen pp. 189 and 190, 1883.

Heat of vaporization of organic compounds, R Schiff, Lieb. Ann. 234, p. 338, 1886, and H. Jahn, Zeit. phys. Chem. 11, p. 790, 1893.

Determination of the heat of vaporization with the ice-calorimeter, Dieterici, Wied. Ann. 38, p. 1, 1889, and H. Jahn, Zeit phys. Chem. 11, p. 788, 1893.

For the special advantages of the ice-calorimetric method see p. 125.

XV. THERMOCHEMICAL CONSTANTS.

General.—So far, the method of mixtures has been usually employed in determining thermochemical values. The unit of heat, therefore, is the calorie at 18° (p. 109).

Inasmuch as the value of the thermal effect measured in small calories (cal.) is usually too large, and the last figure uncertain, it is better to employ as unit a value equal to 100 times that calorie. This large calorie is represented by K, and is approximately equal to the quantity of heat which is necessary to heat 1 gm. of water from 0° to 100°.

Besides that, the calorie of Berthelot should be mentioned, which is equal to 1000 small calories, and is represented by *Cal.*, to distinguish it from *cal.*

The thermal effect is always referred to gram-formula-weight. This is mentioned on account of its dependence upon the temperature. As far as the method of mixtures is concerned, the temperature of the room (18°) comes into consideration.

Of the different methods of notation in use, that of J. Thomsen is preferable on account of its brevity.

The thermal equation,

$$K, Cl, O_3 = 959\ K,$$

means that in the formation of one gram-molecule of potassium chlorate from the elements, 959 large calories of heat are set free (heat of formation) : KCl, O_3 is the thermal effect of the salt when formed from potassium chloride and oxygen, K, Cl, O_3, aq the thermal effect in forming one gram-molecule of potassium chlorate in aqueous solution from the elements, $KClO_3$, aq the thermal effect of dissolving one gram-molecule of potassium chlorate in a definite quantity of water (heat of solution). KOH aq, HCl aq, is the quantity of heat set free in the neutralization of one gram-molecule of potassium hydrate and hydrochloric acid in dilute aqueous solutions (heat of neutralization). The state of aggregation, in case of doubt, is represented by means of indices (H_2O_{gas}, H_2O_l, H_2O_s).

If several reactions are possible between two substances, combinations, and decompositions, the latter are represented by a colon ($HgO : Cl_2$; $SbCl_3 : aq$).

The most important law of thermochemistry is the law of Hess, according to which the thermal effect of any chemical change is the same whether the change consists of one phase or any number of separate phases,—*e. g.* :

$$C, O + CO, O = C, O_2 ;$$

or,—

$$K, Cl = H, Cl. aq + K, O, H, aq + HCl\ aq, KOH\ aq - H_2, O - KCl, aq.$$

1. THE HEAT OF NEUTRALIZATION.

By the heat of neutralization of a monobasic acid and a base is meant the amount of heat evolved when one gram-molecule of the acid and one gram-molecule of the base dissolved in water are mixed. For polybasic acids, as many heats of neutralization are distinguished as there are basicities (H_3PO_4 aq, KOH aq ; H_3PO_4 aq, 2KOH aq ; H_3PO_4 aq, 3KOH aq).

Apparatus.—The use of a mixture calorimeter (Fig. 59) is advantageous. *A* and *B* are two cylindrical vessels, somewhat higher than wide, with a capacity of 1000 c.c. (*A*), and 500 c.c. (*B*) or at least 500 to 250 c.c. As material, platinum and pure or gold-plated silver are to be recommended; for weak acids and bases, nickel-plated brass may be used; glass vessels (p. 112) can be used only for very rough measurements. The outer cylinders *C* and *D*, in which *A*, supported by means of three cork-points, is placed, consist of brass (polished on the interior surface). *C* or *D* is double-walled, and contains air or is filled with water. During the investigation both vessels are provided with covers with suitable openings. The vessel *B* is narrowed below into the tube *r*, which discharges below the upper edge of *A* and can be opened and closed by means of the valve *v*.

As stirring arrangement for *A* and *B*, the stirrer on page 113 is to be recommended, which, for a large number of experiments, can be connected with a turbine (p. 65).

The thermometers in *A* and *B* are graduated to $\frac{1}{50}$ of a degree, and are read by means of a microscope or telescope (after previous

tapping) to 0.002°. From time to time these thermometers should be compared by immersing the two simultaneously in a liquid; the necessary correction is to be applied.*

On the determination of the water-equivalent of the vessel *A*, stirrer and thermometer, see pages 110 and 113. The total water-equivalent amounts to about 5 to 10 gm.

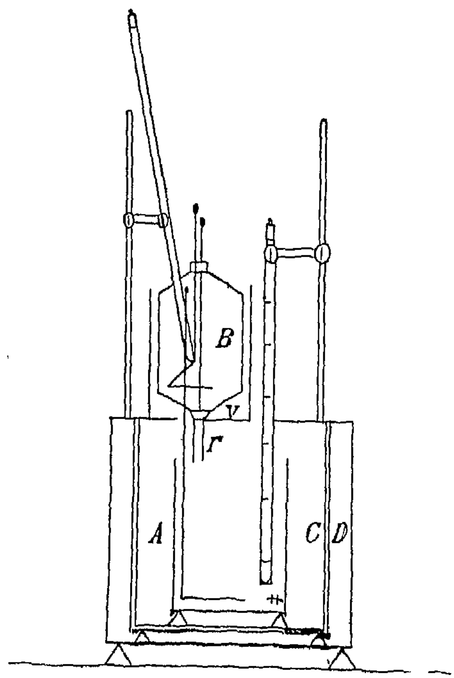

FIG. 59.

A card-board or asbestos screen should be placed between the observer and the calorimeter.

Method of Operation and Calculation.—The observations should be made in a room the temperature of which is as constant as possible. The temperature best adapted is 18° to, at most, 20°.

The solutions for investigation are usually very dilute: ordinarily

* See also J. Thomsen, Therm. Unters. III, p. 341, 1883.

one gram-equivalent of the acid and base in 100 or 200 gram-molecules of water ($NaOH + 100$ or $200\ H_2O$; $H_2SO_4 + 200$ or $400\ H_2O$).

Sometimes still higher dilutions are used, *e.g.*, to prevent precipitation. The use of concentrated solutions should be avoided as much as possible.

It is advantageous to have a simple fractional part of the molecular weight of the solution in the calorimeter. For a solution then, of $NaOH + 100\ H_2O$ (molecular weight $= 1840$ gm.) $\frac{1}{4}$ or $\frac{1}{6}$ of a gram-molecule is used; the solution would then contain 450 or 300 gm. of water. Likewise for a solution of $\frac{1}{2}H_2SO_4 + 100H_2O$, $\frac{1}{4}$ or $\frac{1}{6}$ equivalent should be placed in the calorimeter.

The solutions are best weighed off in the calorimeter vessels. It is immaterial which of the two vessels A and B contain the acid or base.

At the beginning of the investigation, the two solutions are constantly stirred until their temperature change amounts only to a few thousandths of a degree in several minutes. Then, after reading the temperature, the valve v is opened. The adjustment of the temperature usually takes place within one minute (especially if the temperature is not lowered). If the temperature differs not more than $1°$ from the temperature of the surroundings, it will remain constant for several minutes.

A correction for the loss of heat by radiation, then, is unnecessary; otherwise see page 115.

If a and b are the weights in grams of the water in the solutions (usually $a = b$) contained in A and B, and t_a and t_b the temperatures at the time of the mixing, τ the final temperature of the system, w the water-equivalent of the parts of the apparatus which come into consideration, and $\frac{1}{p}$ the fraction of a gram-molecule which was dissolved in the solutions contained in A and B, then the heat of neutralization N for 1 gram-molecule of acid and base, in large calories (p. 132) $= K$ is given by the expression:

$$N = \frac{p}{100}\left[b\,(\tau - t_b) + (a + w)\,(\tau - t_a)\right].$$

The specific heat of the solution is here taken equal to unity,

which can be done for the dilution under consideration. The error amounts to less than one per cent. See Tables of Specific Heats: Thomsen, Therm. Unters. 1, p. 46, 1882.

Special Rules for Determining Heats of Neutralization.—When it is required to determine the heat of neutralization of a polybasic acid with a monovalent base, or a polyvalent base with a monobasic acid, the thermal effect is calculated for the neutralization of each of the basicities separately.

Precipitations should be avoided if possible; in case a precipitate is formed, the heat of precipitation (p. 138) must be subtracted from the heat of neutralization For incomplete precipitates, the necessary correction is calculated.

The state of aggregation of the substance acting on another should be specified in cases where doubt is possible; if the acid or base is a solid or gas, the correction for the heat of fusion and solution or the heat of absorption (p. 138) must be applied as far as possible; *e.g.*, from the thermal effect ($2NaOH\,aq, CO_2$), which refers to the neutralization of aqueous sodium hydrate with gaseous carbonic acid, must be subtracted the thermal effect (CO_2, aq); *i.e.*, the heat of absorption of carbonic acid, thereby the true heat of neutralization ($2NaOH\,aq, CO_2\,aq$) is obtained.

If for any reason the direct mixture of an acid and a base is not possible, or a control determination is desired, an indirect determination is made either by the decomposition of a salt with an acid or base or by the interaction of two salts (see p. 133, law of Hess).

The heat of neutralization of barium hydrate with chloric acid can be calculated from the equation:

$$BaCl_2O_6\,aq, H_2SO_4\,aq = BaO_2H_2\,aq, H_2SO_4\,aq - BaO_2H_2\,aq,\ 2HClO_3\,aq.$$

Likewise we have the equation:

$$BaCl_2\,aq, K_2SO_4\,aq = BaO_2H_2\,aq, H_2SO_4\,aq - BaO_2H_2\,aq, 2HCl\,aq - 2KOH\,aq, \\ H_2SO_4\,aq + 2KOH\,aq, 2HCl\,aq.$$

When four values are known the fifth can be calculated.

Tables of heats of neutralization, see Thomsen, Therm. Unters. 1, pp. 295 and 418, 1882; and Berthelot, Méc. chim. 1, p. 384, 1879. Influences of temperature, Thomsen, Therm. Unters. 1, p. 68, 1882.

Measurement of the heat of neutralization with the ice-calorimeter, Jahn, Wied. Ann. 43, p. 307, 1891.

2. HEAT OF SOLUTION.

By the heat of solution is meant the thermal effect produced by dissolving one molecular weight of a substance in a given number of molecules of water (or other solvents)

The heat of solution is sometimes positive and sometimes negative. It varies with the quantity of water used, and likewise with the temperature. Both must therefore be specified.

Apparatus and Method of Operation.—The mixture calorimeter described on page 112 may be employed. The same can be provided with a Beckmann thermometer. Glass apparatus (p. 112) is sometimes used for rough determinations.

In regard to the quantity of substance to be dissolved, see remarks on page 135. Here also a rational fraction of a gram-molecule $= \frac{1}{p}$ is dissolved in a quantity of water, so that the solution contains 200 or 400 gram-molecules of water to one equivalent of the substance.

$\frac{1}{p}$ gram-molecule of the substance to be dissolved and the corresponding quantity of water $= a$ gm. is weighed off in the calorimeter.

If w is the water-equivalent (pp. 110 and 113), τ the final temperature of the system, and t the initial temperature, then the heat of solution L, measured in large calories, is:

$$L = \frac{p}{100}(a + w)(\tau - t)$$

The specific heat of the solution is here placed equal to unity. This can be done only for dilute solutions, not for concentrated. For such cases, see Tables of Specific Heats, Thomsen, Therm. Unters. 1, p. 46, 1882, and Berthelot, Méc. chim 1, p. 495, 1879.

In regard to the method of operation, it is only necessary to add to what was said on the method of mixtures (p. 112) that the investigation is commenced when the substance to be dissolved has assumed the temperature t of the water in the calorimeter. To accomplish this, the substance is introduced into the water of the calorimeter, in a weighed quantity, in a small, thin-walled glass bulb. After the temperature has become settled, the glass bulb is

broken by means of the stirrer or two pieces of glass introduced into the calorimeter.

The accuracy of the results depends upon the rapidity with which the substance dissolves. If the investigation continues for several minutes, or if the increase or decrease of temperature amounts to several degrees, the loss of heat by radiation must be taken into account according to page 115.

Substances for investigation: $1NaCl + 100H_2O$, heat of solution $= -11.8\,K$; $[MgSO_4 + 7H_2O] + 393H_2O$, heat of solution $= -.38\,K$ (according to Thomsen).

For difficultly soluble substances, compare the special methods of Thomsen, Therm. Unters. II, p. 232, 1882; III, pp. 328 and 341, 1883.

Sometimes the heat of precipitation, numerically equal to the heat of solution, is determined; *i. e.*, the quantity of heat which is set free in the separation of a gram-molecule of a substance from a solution. By a suitable reaction, a substance is formed in a solution (1) at such a dilution that no precipitate is formed, (2) so that the substance is precipitated as completely as possible. The heat of solution is calculated from the difference of these two thermal effects.

If the heat of solution of a substance containing water of crystallization is determined, care should be taken that the water content slightly exceeds the normal water of crystallization, rather than that a loss of the water of crystallization takes place. The quantity of solvent is then chosen so that, if the substance contains n molecules of water of crystallization, $200 - n$ or $400 - n$ molecules of water are used for each equivalent of the substance ($Na_2SO_4 + 10H_2O$, $390H_2O$). See Heat of Hydration, page 140.

The state of aggregation of the substance to be dissolved must be taken into consideration, and if necessary should be specified.

For gases, the heat of absorption is to be considered; *i. e.*, the quantity of heat set free when one molecular weight of a gas is dissolved in a constant quantity of water.

Thomsen, Therm. Unters. I, p. 257, 1882. Tables of heats of solution and absorption, Thomsen, Therm. Unters. III, p. 195, 1883, and Berthelot, Méc. chim. I, p 394; p. 511, 1879. Influence of temperature on the heat of solution, Thomsen, Therm. Unters. I, p. 70, 1882.

Use of the ice-calorimeter for determining the heat of solution, Scholz, Wied. Ann. 45, p. 195, 1892.

3. HEAT OF DILUTION.

By the heat of dilution is meant the quantity of heat which is set free or absorbed when a solution is further diluted with the solvent. The heat of dilution is referred to as HCl 50 aq, 50 aq; HCl 25 aq, 75 aq; HCl 40 aq, 60 aq, etc., and the quantity of water is chosen usually so that the quantity of water of the solution and the final quantity of water make a constant whole number, as HCl n aq, 100 — n aq.

The heat of dilution may be determined in a manner similar to that for the heat of solution, in that the solution to be diluted is introduced in a small closed tube, which is broken as soon as the temperature becomes constant.

The calorimeter (Fig. 59, p. 134) is also frequently used. The water is usually placed in A and the solution in B. For higher concentrations a special arrangement is sometimes necessary. The quantity of solution used is so measured that it contains a simple fractional part $= \frac{1}{p}$ of a gram-molecule (see p. 135).

For the method of operation see the same page; the loss of heat by radiation, however, is generally taken into consideration according to page 115.

If t_a is the temperature of the water, t_b the temperature of the solution, τ the corrected final temperature of the mixture (the specific heat of which is c), w the water-equivalent (pp. 110 and 113) of the lower vessel A (with the stirrer and thermometer), a the weight of the water, b the weight of the solution to be diluted, and $\frac{1}{p}$ the fraction of a gram-molecule of dissolved substance contained in the solution, then the heat of dilution V, measured in large calories (K), is:

$$V = \frac{p}{100}\left[(\tau - t_b)\big((a + b)\,c + w\big) - (t_a - t_b)(a + w)\right].$$

For accurate determinations, therefore, of the heat of dilution, the specific heat of the resulting solution must be known. See Tables of Specific Heats, Thomsen, Therm. Unters. 1, p. 46, 1882; Berthelot, Méc. chim. 1, p. 495, 1879; and Landolt-Börnstein's Tabellen, p. 185, 1883.

The heat of dilution can, however, be accurately determined for a solution the specific heat of which is unknown. It is then only necessary that the temperature of the water in *A* be such that the temperature of the solution after dilution is the same as that of the original solution in *B*. See Thomsen, Therm. Unters. III, p. 43, 1883. Substances for investigation: $[NaCl + 10H_2O] + 40H_2O$; $V = - 5.3\ K$; $[MgSO_4 + 20H_2O] + 30H_2O$, $V = + 2.8\ K$ (according to Thomsen). Tables of heats of dilution: Thomsen, Therm Unters. III, p. 37, 1883; influence of temperature on the heat of dilution, *ibid.* I, p. 80, 1882.

4. HEAT OF HYDRATION.

The heat of hydration is the quantity of heat set free when one gram-molecule of a substance combines with a definite number of molecules of water to form a hydrate.

The heat of hydration is obtained by subtracting the heat of solution of the substance containing water of crystallization from the heat of solution of the anhydrous substance,—*e.g.*, $MgSO_4, 7H_2O = MgSO_4$, aq — $MgSO_4, 7H_2O$, aq. The method, therefore, is that for determining the heat of solution (p 137).

The thermal effects for the taking up of the first, second, third, etc., molecule of water of crystallization are often very different. The thermal effect, therefore, is frequently determined for each molecule of water separately.

If L_0 is the heat of solution of the anhydrous substance, L_m the heat of solution of the compound with the maximum water of crystallization, L_n the heat of solution of the substance with n molecules of water, and m the maximum number of molecules of water, then

$$\frac{L_0 - L_m}{m} \text{ and } \frac{L_0 - L_n}{n}$$

are the average thermal effects corresponding to the total number m and the first n molecules of water. If the two values are equal, it is evident that all the molecules of water are combined with equal quantities of heat.

The partial and complete dehydrations are accomplished in a drying oven. It is better that the substance with the maximum

water of crystallization should contain a slight excess rather than a deficiency of water. In regard to the quantity of water used for the solution, see page 138.

The following example will serve as an illustration:

Thomsen found for the solution of $1Na_4P_2O_7$ in 800 mol. H_2O:

	Molecules of Water of Crystallization $= n$.	Heat of Solution of the Salt $Na_4P_2O_7$, nH_2O.	Mean Thermal Effect for the Taking up of n Molecules of Water.
$1Na_4P_2O_7$, . .	0. H_2O	118.50 K	
$1Na_4P_2O_7$, . . .	1.480 H_2O	82.49 K	36.01 : 1.480 = 24.3 K
$1Na_4P_2O_7$, .	5.074 H_2O	1.23 K	119.73 : 5.074 = 23.6 K
$1Na_4P_2O_7$, . . .	5.962 H_2O	21.39 K	139.89 : 5.962 = 23.5 K
$1Na_4P_2O_7$, . . .	10.0 H_2O	116.70 K	235.20 : 10.0 = 23.5 K

The thermal effects, therefore, for the separate molecules of water for sodium pyrophosphate are approximately equal; this is not the case with most salts.

Tables of heats of hydration: Thomsen, Therm. Unters III, p. 187, 1883, and Berthelot, Méc. chim. I, pp. 359 and 392, 1879.

5. HEAT OF COMBUSTION.

The heat of combustion is the quantity of heat set free in the complete combustion of one gram-molecule of a substance.

The Calorimetric Bomb (Method of Berthelot).*

Principle and Calculation.—The substance is placed in a suitable vessel—a calorimetric bomb—and surrounded by an atmosphere of oxygen at a suitable pressure. After introducing the bomb into the calorimeter, the substance is burned in the nature of an explosion induced by electrical means.

If t is the initial temperature in the calorimeter, τ the final temperature of the same, P the weight of the water in the calorimeter, w the total water-equivalent of the calorimeter, stirrer, thermometer, and bomb, p the weight of the substance burned in the bomb, and

* Berthelot, Ann. chim. phys. (5) 23, p. 160, 1881; Compt. rend 115, p. 201, 1892; and Stohmann, Jour. prakt. Chem. N. F 39, p 503, 1889.

m the molecular weight of the substance, then the quantity of heat evolved, measured in large calories (K),

$$= \frac{1}{100} (P + w) (\tau - t),$$

and the heat of combustion for constant volume is

$$Q_v = \frac{m}{100\,p} (P + w) (\tau - t).$$

The heat of combustion is usually referred to constant pressure.

This reduction of the heat at constant volume to constant pressure at 18° can be made, for solids and liquids of the formula $C_mH_nO_r$, according to the formula:

$$Q_p = Q_v + 0.291 \left(\frac{n}{2} - r\right),$$

where Q_p and Q_v are the heats of combustion at constant pressure and constant volume, and n and r the number of hydrogen and oxygen atoms.

The following formula is of general application:

$$Q_p = Q_v + 0.02\,q\,T.$$

q represents the number of gram-molecules of gas which disappear in the reaction, and T the absolute temperature; $0.02 \times 291\,K = 5.82\,K$ must therefore be added to the observed heat of combustion at 18° for each gram-molecule of gas which disappears, and the same number of calories subtracted for each gram-molecule of gas formed.*

Apparatus.—1. *The Calorimeter.*—The calorimeter is placed in the experimental-room, the temperature of which must be carefully regulated.

The inner cylindrical brass vessel (20 cm. high and 15 cm. wide and 500–600 gm. in weight) rests in a larger double-walled vessel of the same material, which is filled to a height of 10 to 15 cm. with water. The two vessels are isolated by means of pieces of ebonite, which are fastened together by means of glass rods. The stirring arrangement (about 200 gm. in weight) may be made of

* Ostwald, Allgem. Chem., 2. Aufl., Bd. II, pp. 81 and 370, 1892; Berthelot, Méc. chim. I, p. 116, 1879; and Ann. chim. phys. (5) 23, p. 168, 1881.

three ring-shaped brass plates, which are firmly fastened together by means of wires, so that the cylindrical discs lie one above the other, and so that the wires are united at the top of, and in the axis of the cylinder.

The stirrer should take up the entire space between the outer wall of the bomb and the inner wall of the calorimeter vessel. For a bomb, therefore, of 10 cm. and a calorimeter of 15 cm. in diameter, the discs should be 10.5 cm. and 14.5 cm. in diameter. The stirrer must be moved uniformly and in a vertical direction. The wires, therefore, at the point where they are joined together, are fastened to a slide which moves in a vertical direction, owing to its being fastened eccentrically on a disc which is rotated by means of a turbine.

This movement must take place so that, for the deepest position of the stirrer, the lower plate must come almost in contact with the bottom, and for the highest position the upper plate must come almost to the surface of the water.

The upper discs of the stirrer are provided with two openings for the introduction of the thermometer.

The (Beckmann) thermometer must be carefully tested. It is graduated to $\frac{1}{50}$ or $\frac{1}{100}$ of a degree, so that, by means of a microscope, it may be read accurately to 0.002°. (The tapping of the thermometer must not be forgotten.) The contrivance which supports the stirring apparatus is fastened to the outer calorimeter mantle.

2. *The Bomb* (Fig. 60).—The bomb consists essentially of a cast-steel vessel *A*, which is closed air-tight by means of the steel cover *B*. The interior of the vessel and cover is lined with platinum. For a bomb with a capacity of 300 cm., about 1200 gm. of platinum and 2700 gm. of steel* should be used, so that, with the addition of the brass contrivance which supports the bomb in the calorimeter, the combined weight amounts to about 4 kgm.

The manner in which the bomb is closed by the cover is evident from the figure.

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* These are the approximate weights for the bomb of Stohmann; Berthelot's bomb of 200–250 cm. capacity requires not more than half this quantity of platinum. The calorimeter is correspondingly smaller.

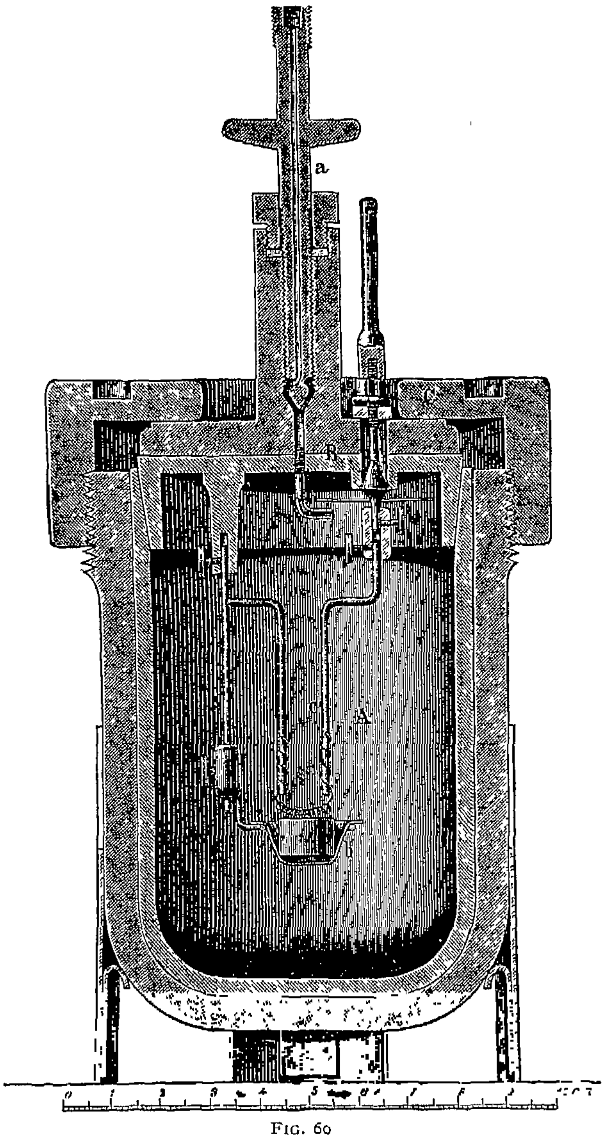

FIG. 60

The platinum edge of the cover is carefully slipped into the conical opening of the vessel *A*. The cover is pressed down firmly by means of a large screw, which surrounds and screws tightly to the outside of the vessel. In the upper surface of the screw are two holes, in which are placed two iron pegs (not shown in the figure). By means of these the screw *C* can be tightly turned.

The bomb, after filling with oxygen and the substance, is firmly fastened in a steel ring consisting of two halves covered with white lead, and tightly closed by means of the steel pegs. Previously, however, the upper portion of the conical part of the cover should be carefully covered with grease.

The contrivance *a* in figure 60 is used for filling the bomb with oxygen and the gases to be combusted; likewise for the subsequent removal of the gases resulting from the combustion.

It consists of a hollow, thick-walled, steel cylinder, which can be so adjusted by means of the screw arrangement, which is from 3 to 4 cm. long, that the conical valve below is either tightly closed, or that the opening for the outflow and inflow of gases is in direct communication with the short platinum tube, bent at a right angle, which extends from the lower end of the screw arrangement into the interior of the bomb.

When the screw is turned down as far as possible, the bomb is closed air-tight; half a turn upward then is sufficient to allow the gases to enter.

For solid and liquid substances there is situated in the interior of the bomb a small platinum vessel *b* resting in a platinum ring, which can be raised or lowered on a heavy platinum wire, which is fastened to the cover. This arrangement is necessary so that the substance can be placed just below the wires *c c'*, by means of which the combustion is induced.

Inasmuch as the wire *c*, which is firmly soldered to the platinum support of the vessel, is connected with the bomb, thus forming a conductor, *c'* must be carefully insulated. This can be accomplished by means of a small platinum cone which is connected with *c'* and inserted, air-tight, in the cover. The cone is covered with thin black rubber. (A shellac covering is less durable). A small ivory ring, at the outlet through the cover, is shoved over the platinum rod which supports the cone; the ring is made air-

tight by means of a screw, which simultaneously exerts a pressure on the rubber, thus forming a very thin membrane. Care should be taken (especially before the first combustion) that small pieces of rubber do not fall into the interior of the bomb during the tightening of the screw; otherwise the pieces must be removed. The danger from the burning of rubber can be prevented by placing a piece of mica, through which a hole has been bored, between the cover and the rod of the cone.

The burning of the substance is brought about by means of fine iron wire (Blumendraht) which is melted off at a glowing heat. The wire is rolled spirally on a strong needle and is fastened to *c* and *c'* by means of fine platinum wires. In order to remove the thin coatings of non-conducting iron oxide which may be formed on *c* and *c'* during the combustion, the ends of the wires are immersed from time to time in molten potassium bisulphate.

As equal lengths of the iron wire have approximately equal weights, a correction may be easily calculated for the iron which burns to iron oxide; equal lengths of wire = 5 cm. are always taken so that the weight (about 0.006 gm.) need be determined only once.

The wire is heated by means of three Bunsen chromic-acid elements; the glowing particles of oxide from the burning wire fall upon the substance immediately under the wire and start the combustion.

3. *Contrivance for the Introduction of Oxygen.*—The oxygen to be used should be free from chlorine and carbon monoxide. Any chlorine present may be removed by passing the gas through potassium hydrate, while the carbon monoxide can be best removed by means of palladium chloride. Combustible gases and small particles of oil from the pump are rendered harmless, in that the oxygen is first passed through a copper tube heated in a combustion furnace, and after cooling is introduced through a narrow spiral tube into the bomb. The main portion of the oil from the pump is held back mechanically, in that a large number of fine wire gauzes are placed at very small distances from each other in a metallic cylinder immediately behind the pressure-valve of the pump. The presence of carbonic acid causes no inconvenience. To avoid corrections, the oxygen should not be dried, but should be saturated with water vapor.

It is very convenient to make use of the commercial oxygen tanks, in which the oxygen exists under a pressure of about 120 atmospheres. The gas can best be pumped from an ordinary gasometer into the calorimetric bomb by means of a good suction- or pressure-pump; the tube of the pump should be surrounded by a mantle of flowing cold water; otherwise the heat from friction may occasion explosions between oil and compressed oxygen.

The pump should be provided with a manometer which indicates $\frac{1}{10}$ atmospheres.

Details of the Method of Operation.—The water-equivalent of the calorimeter and stirrer (pp. 110 and 113) can be determined simply by multiplying the weight in grams by the specific heat of brass = 0.094. However, it is perhaps better to determine the specific heat of the particular kind of brass used in the calorimeter. The weight of only that portion of the stirrer which is immersed for the highest position in the water of the calorimeter can be taken into account.* A further determination of the water-equivalent of the calorimeter and stirrer, so far as the latter comes into account, may be made by quickly pouring a quantity of water, from a protected vessel heated to a constant temperature (about 60°), to the necessary height in the calorimeter (containing the stirrer and thermometer). The water-equivalent of the metallic portions (including the thermometer) can be calculated from the quantity of heat given up to these portions, by multiplying the temperature difference of the water by its weight and dividing the product by the temperature elevation of the metallic portions. For the dimensions and weights given for the calorimeter and stirrer, the combined water-equivalent amounts to about 60 to 70 gm. For the water-equivalent of the portion of the thermometer immersed see also page 114.

The water-equivalent of the bomb with brass foot can be accurately determined by several methods:

1. The number of grams of steel, platinum, and brass used are

* A direct and perhaps more accurate way of determining the water-equivalent of apparatus, see Stohmann, Jour. prakt. Chem. 39, p. 528, 1889.

multiplied by the corresponding specific heats (specific heat of steel $= 0.1097$, platinum $= 0.0324$, and brass $= 0.094$).

2. The bomb, together with the stirrer, can be introduced into the calorimeter vessel, and water, previously heated to exactly t° (60°), added until the bomb is immersed. The sum of the water-equivalents of the bomb, calorimeter and stirrer can then be calculated (see p. 147).

3. The bomb is heated for some time in a water-bath to about 30° until the temperature becomes constant to about $\frac{1}{100}$ of a degree; it is then introduced as quickly as possible into the calorimeter containing sufficient water at a constant temperature equal to that of the room. The temperature elevation of the contents of the calorimeter, multiplied by the total water-equivalent of the same, and divided by the decrease in temperature of the bomb, gives the water-equivalent.

A small correction is to be introduced on account of the water which adheres to the bomb during the heating. The approximate weight of the same is determined from several weighings of the wet bomb. If the outer surface of the bomb is covered with a trace of grease, the adhering water amounts to only a few grams, and it is necessary simply to subtract the number of grams from the observed water-equivalent of the bomb.

The water equivalent of the bomb, which for the weight given would amount to about 350 gm., can be determined by the preceding methods to from 1 to 2 gm.

In carrying out the experiment, the bomb is immersed in the water so far that only the handle of the closing screw *a* remains uncovered. The calorimeter, for the dimensions of the apparatus given, should contain about 2500 gm. of water.

The preceding is subject to some variation, depending upon whether the substance to be combusted is a solid, liquid, or a gas.

A large excess of oxygen must be used in the case of solids. The oxygen is pumped into the bomb until the manometer shows a pressure of about 25 atmospheres. A bomb of 300 c.c. capacity should contain from 10 to 11 gm. of oxygen. The quantity of substance to be burned is so chosen that, after the combustion, the remaining oxygen occupies at least one and a half times the volume

occupied by the gases formed in the combustion. For 10 gm. of oxygen usually 3 gm.; *i. e.*, 30 per cent. of the quantity may be used in the combustion; then, on the assumption of complete combustion to CO_2 and H_2O, the quantity of substance to be used in the combustion can be calculated (*e. g.*, 1 gm. of naphthalene corresponds to about 3 gm. of oxygen).

If one is not certain that the combustion is complete, the combustion gases are slowly conducted through a solution of palladium chloride. The least quantity of CO will produce a black precipitate, and may thus be detected.

For many substances, in oxygen under a pressure of 25 atmospheres, the combustion is not induced by the molten iron wire. The combustion may be facilitated in such cases by covering the substance with a small weighed quantity of an easily combustible substance (a few grams of naphthalene); the heat set free in the combustion of that substance will start the combustion in the original substance. Of course, a small correction must be introduced in this case. The heat of combustion of the substance used to induce the reaction is multiplied by the quotient of the weight used, divided by the molecular weight, and the product subtracted from the total heat of combustion. Only a few substances (oxalic acid, mellitic acid) show difficulties in their combustion according to this method. Solid substances should be made as compact as possible for the combustion—in the form of pastilles, or, when the substance can be fused without decomposition, in the form of a solidified fusion.

A steel arrangement, constructed on the plan of the diamond mortar used in crushing minerals, is used as a pastille press. The inner part has a suitable width and the bottom can be removed. The substance is previously weighed. A press of the hand is frequently sufficient to produce the necessary compactness in the pastille.

If the substance to be combusted is a volatile liquid (aldehyde, ether, benzene, etc.), a correction relative to the heat of vaporization must be introduced, for a portion of the substance is combusted in the gaseous and a portion in the liquid condition. For the calculation of this correction, see Stohmann, Jour prakt. Chem. 40, pp. 78 and 342, 1889.

The heat of combustion has reference entirely to the liquid state.* The liquid is introduced into a small glass globe, which is closed by fusion, and which is so thin-walled that a slight movement of the bomb, immediately before the beginning of the experiment, is sufficient to break the globe. Berthelot, Pierre, and Matignon,† however, have proposed that the liquid be contained in a small platinum capsule, which is surrounded by an envelope of gun-cotton, closed at the top by means of a thread of the same material.

Gaseous substances should be mixed with no more oxygen than is necessary for their combustion to carbonic acid and water. At all events, only a very slight excess of oxygen is to be recommended (about 1 per cent). The combustion in this case is almost always complete for atmospheric pressure. The gases formed in the combustion should be tested for carbon monoxide. The weight of the combusted gas may be determined at the end of the experiment by slowly conducting the gases contained in the bomb through dissolved and over solid potassium hydrate. The apparatus is most conveniently filled (in case it is not necessary to mix the gases outside of the bomb) as follows: After exhausting the bomb, the gas to be combusted is first introduced, then the volume of oxygen necessary for the combustion is calculated, and the same, by observing the pressure indicated by the manometer, is introduced into the bomb in slight excess.

The combustion of the substance introduced into the bomb takes place almost instantaneously. Some minutes (three to four), however, are required for the equalization of the temperature in the calorimeter. The experiment is begun after the bomb has remained for some time in the calorimeter. The temperature of the apparatus at the beginning of the experiment should be about as much below the temperature of the room as it is above the temperature when the experiment is completed. The temperature

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*For the comparison of the heats of combustion of different substances it is necessary to refer them to the same state (better, the gaseous state). Then the heats of fusion and evaporation must be considered. See Ostwald, Lehrb. Allgem. Chem., 2. Aufl., Bd. II, p. 371, 1892.

† Berthelot, Compt. rend. 115, p. 201, 1892.

elevation usually amounts to several degrees. The influence of radiation, therefore, should be taken into account according to page 115.

From the observed thermal effect the heat of combustion of the substance is calculated according to page 142. First of all, however, small corrections are to be deducted from the number of calories calculated from the experiment.

1. If a is the weight in grams of ferrous oxide formed by the burning of the spiral, and if, according to Berthelot, the oxidation of 1 gm. of iron to ferrous oxide sets free 16.01 K of heat, then a 16.01 K must be deducted from the observed thermal effect.

2. The nitrogen of the air which was not removed before the introduction of the oxygen, and which still remains in the bomb, is burned to nitric acid. The acid formed is taken up by the condensed water, and, after being completely washed from the bomb, its quantity can be determined by titration (dilute sodium carbonate and methyl-orange). For each gram-molecule of aqueous nitric acid (63 gm. HNO_3 aq) formed 143 K, according to Berthelot, are to be deducted.

3. A bomb of 300 c.c. capacity, and at a pressure of 25 atmospheres, contains somewhat more than 10.5 gm. of oxygen. This oxygen must go through the temperature change. As the specific heat is 0.2175, the number of grams of oxygen (10.5) must be multiplied by this number, and the product, which is the water-equivalent of oxygen, must be added to the total water-equivalent of the colorimeter and bomb.

The sum of all these corrections has only a slight influence on the result.

The correctness of the bomb should next be tested, naphthalene being used in the combustion.

The quantity of heat set free in the combustion of 1 gm. naphthalene, at constant volume, according to the investigations of Berthelot, is 96 94 K.

(The values for nineteen determinations vary between 97.43 and 96.51 K.)

The bomb of Berthelot, Stohmann, and others is made in Paris (by Golaz).

The high price of the apparatus, owing to the large quantity of

platinum used in its construction, has hindered somewhat its introduction into the laboratory.

Mahler * has recently described a bomb which is analogous to that just described, and made of half-tempered steel. The interior, instead of being covered with platinum, is furnished with a layer of strong enamel, which must be renewed occasionally. This bomb can be used not only for technical, but also for scientific purposes. Other investigations in this direction, however, are desirable.

On heats of combustion, see Thomsen, Therm. Unters., Bd. IV, p 1; Ostwald, Allgem. Chem. II, p 361, 1892; Armstrong, Phil Mag. (5) 23, p. 73, 1887; Brühl, J. pr. Chem. (2) 35, pp. 181 and 209, 1887; Thomsen, Zeit. phys. Chem. 1, p. 369, 1887, and 7, p. 55, 1891; Dieffenbach, *ibid* 5, p. 566, 1890. Tables of heats of combustion: Stohmann, Zeit. phys. Chem. 2, p. 29, 1888; 6, p. 335, 1890, and 10, p. 410, 1892, *ibid.*, Literature on heats of combustion. Determination of heats of combustion with the ice-calorimeter: Schuller and Wartha, Wied. Ann. 2, p. 371, 1877.

Heat of Formation.—The heat of formation of an organic compound,—*i. e.*, the quantity of heat set free or absorbed in the formation of 1 gram-molecule of the substance, can be calculated from the heat of combustion of the compound. The calculation can be made according to the principle of Hess, by subtracting the heat of combustion of the compound from that of its elements. We have then:

$$C, H_4 = C, O_2 + 2(H_2, O) - CH_4, O_4;$$

or, in large calories K:

$$223 = 976 + 2 \times 683 - 2119.$$

See, among others, Ostwald, Allgem. Chem. II, p. 215, 1892; Berthelot, Méc. chim. 1, 329, 1879.

* Mahler, Compt. rend. 113, p. 774, 1891.

XVI. CRYSTAL MEASUREMENTS.

1. THE REFLECTION GONIOMETER OF WOLLASTON.

Principle.—The goniometer is used chiefly for measuring the angles of crystals,—*i. e.*, those angles which the crystal faces form with each other.

Let the angle which two crystal faces form with each other be represented by $a = o\ n\ m$ (Fig. 61). E is a small mirror, so placed that the image of a suitable object at F, when viewed past the edge of the crystal by the eye situated at A, will appear in the direction $A\ E$. The crystal is then placed in such a position ($o\ m\ n$) that the image of F reflected from the crystal face $o\ n$ appears in the same direction $A\ n$ as the image formed by the mirror E. For this position of the crystal the two images of F reflected from the crystal surface $o\ n$ and the mirror E to the eye of the observer coincide. The crystal is then rotated about the crystal edge n as axis until the two images again coincide, when the crystal will have rotated through the angle $a' = 180° - a$ and taken the position $n\ o'\ m'$ (Fig. 61). The image of F, in this case, is reflected from the surface $n\ m = n\ m'$. The desired angle then is $a = 180° - a'$.

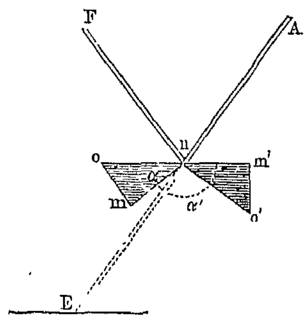

FIG. 61.

Apparatus I.—The apparatus in its simplest form is represented in figure 62.

A circle E graduated to half degrees is provided with a vernier (p. 218), and is movable about the axis G. The instrument is provided with a double axis. If the knob G is turned, the circle E and also the jointed arrangement $K\ L\ M$, which carries the crystal, are rotated. If, however, the inner axis is turned by means of the knob J, the crystal support alone is turned. The graduated

circle may be firmly clamped by means of the pressure screw *U T S*.

The crystal *a* is fastened in a suitable position on the small disc *Q* by means of wax. The adjustment of the same (p. 155) is made possible, first, by the fact that the axis *O* which carries the disc *Q* may be turned in its support *N* by means of the knob *P*;

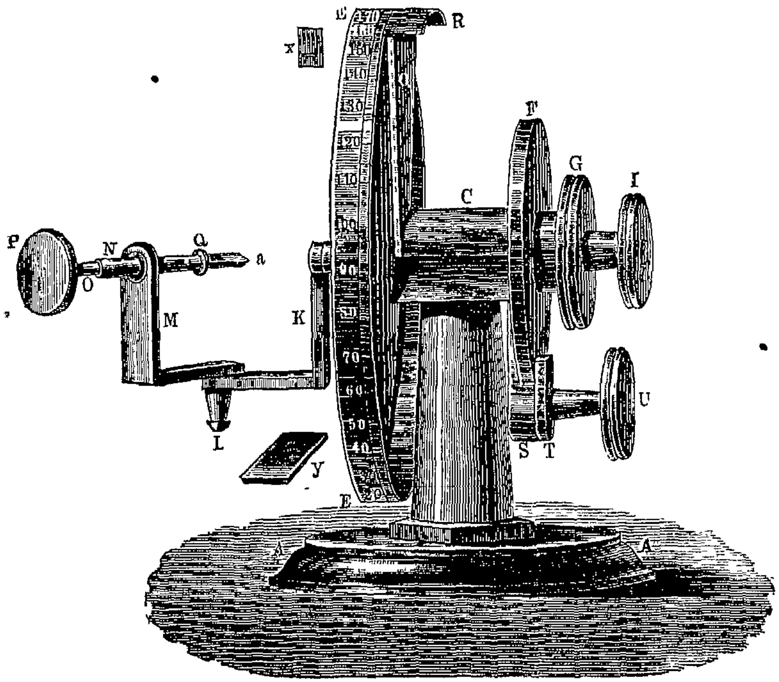

FIG. 62

and, second, by the fact that the arrangement *M L K* is movable at the joints.

Y represents a small mirror which is usually fastened to the foot-plate *A* of the instrument, and is movable about an axis. For a definite position of the mirror the image of a suitable object is visible.

As signal, use may be made of a mark *x* on the window or (if not too near) the cross-bars of a window, the edge of a roof, etc.

Or the window may be darkened and then, at a sufficient distance, provided with a signal, which is a cross-formed slit about 5 cm. long and 0.5 cm. broad, and which is lighted by means of a gas-flame.

Method of Operation.—The apparatus is set up so that the plane which passes through the middle of the signal on the window and perpendicular to the plane of the window is parallel to the graduated circle *E E*. If the mirror *y* is fastened to the foot-plate so that the edge next to the window is parallel to the axis of the measuring circle, then, for the proper adjustment of the instrument, the image of the horizontal bar of the window must be parallel to the same edge of the mirror.

The crystal is fastened to the small disc *Q* by means of wax, so that the edge to be measured, for a suitable adjustment of the joint *L*, falls as nearly as possible in the line of prolongation of the axis of the measuring circle. To facilitate the centering of the crystal the axis *K* should be moved in a slide (not shown in Fig. 62, see p. 157). If the crystal is approximately centered, then, on rotating the knobs *G* or *J* through 360°, the edge to be measured should be displaced from its position only very slightly.

The crystal must then be adjusted. For this purpose the mirror *y* is placed so that the horizontal and vertical bars of the window are visible in the middle of the field of view. If the eye is placed near the approximately centered crystal, then, on rotating the knob *J*, the image of the window-bars reflected from the mirror is seen in the two crystal surfaces, the angle between which is to be measured. If the horizontal and vertical bars of the window appear inclined in the image from the crystal, and at the same time appear normal in the mirror and parallel to the edges of the mirror, the adjustment is inaccurate.

The image then reflected from the crystal and that reflected from the mirror *y* are not brought to perfect coincidence on rotating *J*. If the attempt be made to perfect the adjustment by turning the knob *P* on its axis or by a movement of the jointed contrivance *K L M*, it will be seen in most cases that a movement of either of these is not sufficient of itself to cause the images from the two crystal faces to appear in the same direction as that from the mirror. By combining these two movements, however, such an adjustment, after a little practice, is readily made.

After the adjustment has been made, it is only necessary to determine the angle through which the divided circle must rotate in bringing the images from the two crystal faces successively in coincidence with that from the mirror *y*. The observed angle, of course, is the complement of the angle to be measured. During the observations on the two surfaces the eye should remain as nearly as possible at the same position.

With careful adjustment and well-formed crystals, this method is

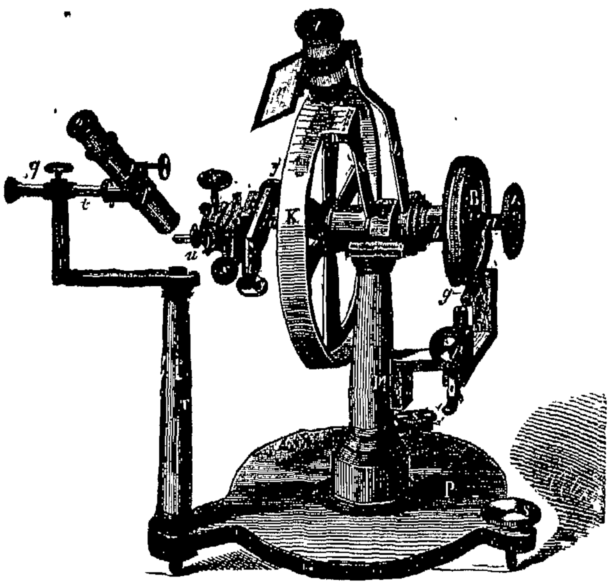

FIG. 63.

accurate to within two to three minutes, which is sufficient for most chemical purposes.

Apparatus II.—A more complete form of apparatus is represented in figure 63.

K is the divided circle with a double axis *A a* and *B b*; *n* is the vernier, which is illuminated through the white paper *r* by means of a small flame and read by means of the microscope *l*; *g* is a micrometer screw, the threads of which turn in the grooves of the circular head *B*, so that the turning of the knob *p*

produces a very slight rotation of B, thereby increasing the accuracy of the adjustment. In order that B may be free to move until approximately adjusted, the knob p is pressed down until the small projection on the spring below enters the opening in the frame i, which holds the screw in the lower position.

The centering and adjustment contrivances are essentially different from those of apparatus 1.

The contrivance for centering consists of two slides lying one above the other and joined to the axis of rotation. By means of the screws $y\,y$ these slides can be moved in parallel planes in directions which are perpendicular to each other. Attached to this is the adjusting apparatus, which consists of two cylindrical sections movable, by means of the screws $x\,x$, in planes perpendicular to each other. A small disc, which serves as the crystal support, is fastened to this contrivance by means of the screw v.

The instrument is also provided with a telescope f with cross-wires fastened to the support T. By means of the screw q and bar t the telescope may be moved parallel to itself, and may also be rotated in a plane perpendicular to t, so that it can be directed exactly toward the axis of the divided circle K.

Method of Operation.—The apparatus is first placed in the proper position, which may be determined by means of a mirror (p. 154) or by means of the telescope.

The telescope, which is provided with cross-wires, is focused by moving the eye-piece o sharply on the signal (the cross-bars of a window at the opposite end of the room, etc.). When the image of the object and the cross-wires lie exactly in the same plane, then a movement of the eye will produce no change in their relative positions.

After the apparatus has been set up, the crystal, which is fastened on with wax, is centered.

For this purpose the telescope is changed to a microscope, either by removing the eye-piece or by placing a lens in front of the objective. The microscope thus formed is focused on the crystal, which can be regarded as centered only when the edge to be measured remains in the same position during the rotation of the crystal.

The crystal is fastened on the disc, so that the edge to be measured is approximately centered. One of the two screws y should

be placed parallel to the telescope. The edge to be measured is then raised or lowered by means of the second screw *y* until it appears in the middle of the field of view. If the axis *A* is now rotated through 90° and the centering screw turned, which is placed perpendicular to the telescope, then the edge must remain in the same position, and therefore be centered.

The adjustment, which is made by means of the screws *x x*, is accompanied by certain difficulties until the operator has had some experience.

The microscope is again converted into a telescope, and, after focusing on the cross-wires and the crystal, the latter is rotated by turning the axis *A a* around the approximately centered edge which is to be measured. The reflected image of the window-bars and the crystal surfaces, if necessary with the help of the screws *x x*, are brought into the field of view in the telescope. The adjustment is inaccurate as long as the directions of the reflected window-bars appear inclined to those of the cross-wires.

The image reflected from the surface, which is parallel to one of the adjustment screws, is brought into the field of view first and the other screw turned until the image coincides with the middle of the cross-wires; the image from the second face is then brought into view and corrected by means of the first screw; the adjustment of the first face is thereby slightly changed, the change being smaller the nearer the face is parallel to the screw. By small subsequent corrections the adjustment is easily obtained, so that the images from the two surfaces, as well as from all other surfaces in the same zone, move along the vertical wire when the crystal is rotated.

After some experience, the operator, regardless of any special rules, can easily make the proper adjustments. The turning and reading of the divided circle is accomplished by means of the knob *B* (see p. 155).

Measurement of Crystal Angles in General.—The crystals should be carefully selected, and the faces which are to be observed should not come in contact with the fingers. They are rubbed off with soft leather and placed on a ball of soft wax, care being taken not to allow the wax to come in contact with any face which is to be measured.

In most cases it is desirable to measure all the angles of a given zone, so far as the condition of the crystal will permit. If the crystal is small, one centering is sufficient for all the measurements of the angles of parallel edges. It is placed, then, in the middle of the zone to be measured; otherwise each edge is to be separately centered, whereby the adjustment remains unchanged. As the accuracy of the results depends upon the condition of the crystal faces, it is desirable, first of all, to project as carefully as possible, on the plane of a paper, a sketch of the crystal, representing the separate faces by the letters *a*, *b*, *c*, etc., and then note down, with the measurements of the faces referred to, the necessary remarks on the condition of the reflected image, etc. From the different measurements of the angles of equal value then is selected a mean value, taking into account the accuracy of the various measurements. In many cases it is advisable to repeat the measurements, using different crystals.

If the crystal face is not uniform, but uneven, curved, or broken, several images, or parts of images, are usually seen in the reflection. The measurements, of course, are then more or less inaccurate, depending upon the sharpness of the image.

Care should be taken, especially for clear, transparent crystals, that the somewhat colored images produced by total reflection from the interior of the crystal and thrown into the field of view of the telescope, are not mistaken for the desired images.

In case of doubt it is only necessary, during the rotation, to observe the crystal with the microscope, formed as previously explained, to determine whether the illuminated surface is turned from or toward the signal, and to determine, therefore, whether the rays from the interior of the crystal or those from the outer surface are reflected into the telescope.

Substances for investigation: Quartz-crystal, prism angle 120°; Iceland spar, rhombohedral angles 74° 44′ and 105° 16′; alum, octahedral angle 109° 28′.

Goniometers with horizontal measuring-circles, see Groth, Phys. Krystallographie II, p. 560, 1885; goniometer as refractometer, *ibid.* p. 585.

2. THE MICROSCOPE, WITH POLARIZING ATTACHMENTS.

Apparatus.—The microscope of Fuess, represented in figure 64, consists, in its essential parts, of the tube *b*, with a system of lenses movable in the double-walled tube *p*, the objective-stage *T*, the mirror below, and the polarization attachments *s* and *r*, which, for investigations in polarized light,* can be fastened above the eye-piece and below the objective-stage.

The objective-table *T* consists of a plate which can be rotated around the vertical axis of the instrument. This plate is graduated in degrees and can easily be moved with the fingers. The plate *i* firmly fastened to the stand below projects over the true stage. On the upper surface of this projection is a mark which serves as an index for reading the divisions on the movable plate *T*.

The tube *r* is firmly fastened to the plate *i*. The polarization-tube, closed by means of a lens, can be shoved into this tube from below. The polarizing-tube contains a Nicol prism (or Prazmowski prism, p. 203), and is rotated in the outer tube *r*, so that the zero point coincides with a definite mark on *r*. For this position the principal section of the prism falls in the plane of the sketch.

Two springs are fastened to the movable plate by means of the screw *q*, in order to hold the substance to be investigated firmly to the stage.

The tube *b* can be moved in a vertical direction on the outer tube *p*.

The instrument is roughly adjusted by taking hold of the tube on the edge *f* and pressing down; the finer adjustment is accomplished by means of the micrometer screw *m*. The head of this screw is usually graduated, thus making it possible to measure the vertical movement of the microscope accurately to the thousandth of a millimeter.†

The double-walled tube *p* consists of two tubes, the inner of which can be turned through a small angle by means of the two

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*On polarized light, etc., see the section Rotation of the Plane of Polarization, p. 203.

† Groth, Physik. Krystallographie, pp. 33 and 648, 1885.

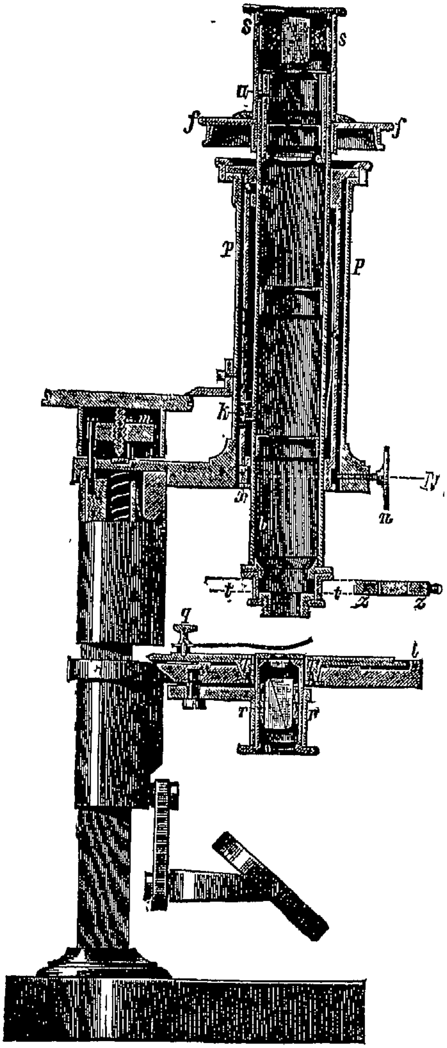

FIG. 64.

screws n and m (Fig. 65), the axes of which are mutually perpendicular.

This makes it possible to center the tube b, a cross-section of which is represented by the innermost double ring (Fig. 65), so that its vertical axis coincides exactly with the axis of rotation of the stage, and hence so that an object brought into the middle of the field of view of the objective does not change its position on rotating the stage—a condition which is necessary for the measurement of plane angles.

Of the different Hartnack objectives 4, 7, and 9, the first, which magnifies, according to the eye-piece, from 90 to 200 diameters, is most frequently used; if the magnification is still to be diminished, the lower lens of the objective must be removed. The instrument is provided with three eye-pieces, the form of which is represented

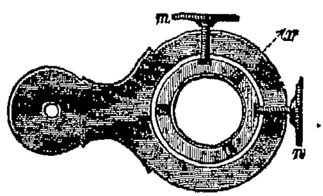

FIG. 65.

FIG. 66.

in figure 66. Between the upper and lower lenses of the eye-piece is a cross-wire or glass micrometer, which can be brought sharply in focus by adjusting the inner tube A. A small screw a of the eye-piece passes through a vertical slit of the tube b, thus making it possible to keep the cross-wires always in the same position, namely, that parallel to the two polarizers when the zero points of their scales correspond respectively with the fixed marks on the tubes. Inasmuch as the position of the principal section undergoes slight change in time, it must be tested from time to time by determining the directions of vibration in a crystal plate (*e. g.*, a rhombohedral crystal of prismatic form).

The tube s for the analyzer can be placed on the eye-piece (see p. 203). This tube, which contains a second Nicol or Prazmowski prism, is provided with a circular scale which can be rotated past the fixed mark on the plate f

If the analyzer and polarizer are adjusted so that their zero points coincide with their corresponding fixed marks, then the two Nicols are crossed and their principal sections coincide with the lines of the cross-wire.

The slit *tt* represented in figure 64 serves as a receptacle for the slide *zz*, which contains a Biot quartz-plate. This plate is introduced to recognize, through the change of tint of the quartz-plate, a slight double refraction in the object, and to determine the directions of vibration in the crystal under investigation.

(*a*) Measurement of Plane Angles.

By plane angle is meant that angle which the two edges of a crystal face, lying horizontally on the objective-stage, form with each other.

For the measurement of this angle the Nicols are unnecessary; the analyzer should always be removed in such cases.

The crystal must be centered as accurately as possible; *i. e.*, the point of intersection of the two edges whose angle is to be measured must be brought into the middle of the field of view, so that on rotating the objective-table it remains in the same position,—at the middle point of the cross-wires (see p. 162). This centering, after a little practice, is accomplished easily and quickly if, when the centering has once been approximately made, the stage be rotated and the axis of the tube suitably adjusted by means of the screws *m* and *n* (Fig. 65), so that the point of intersection of the edges during the rotation of the stage describes each time a smaller circle around the middle point of the cross-wires. By careful movement of the object then the complete centering is easily accomplished.

One of the two edges is then placed parallel to one of the cross-wires, an adjustment which can be accurately made if, instead of bringing the edge and wire into complete coincidence, the edge is placed slightly to the side of the wire.

The position of the stage is then read, and afterward rotated until the second edge is brought into the position which the first had occupied. This angle, through which the objective-stage was turned, is, of course, equal to the plane angle to be measured.

If the measurements are to be made on larger crystals, then the least possible magnification should be used.

See Groth, Phys. Krystall., p. 551, 1885, on the significance of the measurement of plane angles.

(*b*) Testing for Double Refraction and Determination of the Directions of Vibration in Crystals.

The polarizer, analyzer, and cross-wires are given the positions as outlined on page 163. The Nicols are then crossed and the field of view becomes dark.

With this adjustment of the instrument, the objective-table with the object is turned through 360°; if, then, the substance is amorphous, or belongs to the regular system, the field of view will remain dark during the rotation of the object. If, on the other hand, a doubly refracting uni-axial or bi-axial crystal is examined, the uniform darkness for all positions of the stage is observed only for certain few positions of the object—namely, only when the two parallel faces, natural or artificial, of the crystal are perpendicular to the optic axis (or to an optic axis).

On the contrary, for all other positions of a doubly refracting crystal, and therefore in general, the field of view during the rotation of the stage through 360° is dark only in four different positions, which are 90° apart; in the intermediate positions the field appears colored (Groth, Physik. Krystall., pp. 71 and 105, 1885).

If the crystal shows only a slight double refraction, the change of intensity between the darkness and the light is very slight, and it is necessary in such cases to use the Biot quartz-plate (p. 163), which can be shoved into the instrument.

For special exceptions with reference to the above phenomena, see Groth, Physik. Krystall., p. 650, 1885.

If these four positions, for which the plate is dark, have been determined for a doubly refracting crystal which appears colored between crossed Nicols, they represent those positions for which the plane of vibration of one of the two rays in the crystal is parallel to the plane of polarization of the one Nicol. If the direction of the planes of polarization of the three Nicols is given by the position of the cross-wires (p. 163), then the angles which the planes of vibration of the two rays in the crystal plate form with the crystal edges is easily determined. It is only necessary to place a crystal edge parallel to one of the cross-wires (p. 163) and

to determine with crossed Nicols, by rotating the stage, that position which causes darkness in the field of view. A second reading of the divisions on the stage gives directly the angle which the planes of vibration form with the crystal edge. With monochromatic light, the observation will be sufficiently accurate for chemical purposes if, instead of determining the position of maximum darkness, the arithmetic mean is taken of two positions which appear equally removed from this maximum. The determinations should be repeated several times, and the crystal should be carefully examined at the end of each series of observations, to determine whether the crystal edge still remains in the proper position.*

The determination of the vibration-planes is one of the most important measurements in crystallography, and is of itself sufficient in many cases to enable one to distinguish between the crystal forms which come into consideration It is especially necessary to determine whether the vibration-planes form angles with certain crystal edges (inclined extinction), or whether they are parallel to the same (parallel extinction).

The latter case never occurs in the asymmetric system; in the monosymmetric system the parallel extinction occurs only for certain sections of the crystal; while in the orthorhombic system extinction occurs parallel or perpendicular to each of the three crystallographic axes, in the hexagonal and tetragonal systems parallel and perpendicular to the principal axis.†

Substances for investigation: Alum and sodium chlorate (regular); potassium ferrocyanide (tetragonal); iodoform and sodium nitrate (hexagonal); potassium chlorate and ammonium sulphate (orthorhombic); ferrous chloride and ferrous sulphate (monosymmetric); copper sulphate and potassium bichromate (asymmetric).

(c) Investigations in Convergent Light.

The microscope represented in figure 64, page 161, can be used for investigations not only in parallel but also in convergent polarized light.‡

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* Groth, Physik. Krystall., p. 651, 1885.

† O. Lehmann, Krystallanalyse, Leipzig, 1891, pp. 33 and 34.

‡ Groth, Physik. Krystall., p. 69, 1885.

In order to change from measurements in parallel light to measurements in convergent light it is sufficient, in general, to remove the eye-piece and use a higher-power objective; then the characteristic interference figure will be visible instead of the crystal.

The change from one kind of light to the other is still more convenient if a Bertrand lens (an achromatic lens of 3–4 cm. focal length) is attached to the microscope. The removal of the eye-piece is then unnecessary, and it is sufficient for observations in convergent light to place this lens in the opening above the objective (microscope of Fuess, Berlin, Stallschreiberstr., Voigt and Hochgesang, Göttingen).

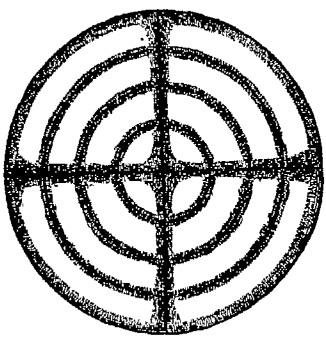

FIG. 67.

When a plate of a tetragonal or hexagonal crystal, cut perpendicular to the optic axis, is observed in convergent polarized light with crossed Nicols, a dark cross with a system of colored rings, the interference figure represented in figure 67 is seen. This characteristic interference figure (see theory of Groth, Phys. Krystall., p. 75, 1885) is elliptical in shape when the surfaces of the crystal section are inclined to the optic axis.

If, on the other hand, a section of a bi-axial crystal (orthorhombic, monosymmetric, or asymmetric), cut perpendicular to the line bisecting the optic axes, is observed, the interference figure appears as represented in figures 68 and 69. The figure has the appearance of figure 68 when the section is placed between crossed Nicols, so that the plane of its optic axes is parallel to the plane of polarization of one of the Nicols. Figure 68 *a* (a black cross with colored lemniscates) is the form shown by thick crystal-plates, while the form figure 68 *b* (a black cross with elliptical rings) is characteristic of thin plates. If the section between the crossed Nicols is turned so that the plane of the optic axes forms an angle of 45° with the plane of polarization of the Nicols, then the form

of the figure changes and takes on the appearance of figure 69, thick plates showing the form 69 *a* and thin plates the form 69 *b*.

The principal difference between uni-axial and bi-axial crystals consists in the fact that the interference figure for the former remains closed on rotating the objective, while for the latter it opens

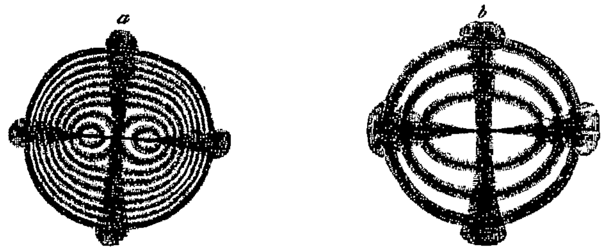

FIG. 68.

and divides into two hyperbolas. For details of these phenomena, see Groth, Physik. Krystall., p. 104, 1885.

Determination of the angle between the optic axes, see Groth, Physik. Krystall., p. 115, 1885; distinction between the positive and negative character of a doubly refracting crystal, *l. c.*, p. 122.

Stauroscopic measurements, *ibid.* p. 618. Cutting, grinding, and polishing crystals, *ibid.* p. 667.

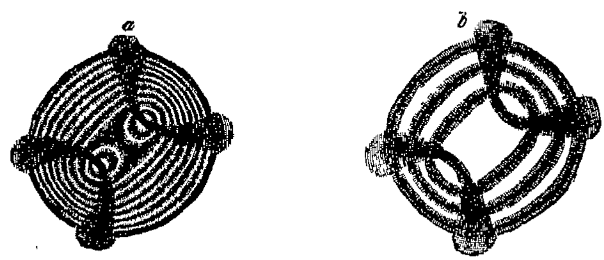

FIG. 69.

Isomorphism, Retgers, Zeit. phys. Krystall. 3, p. 497, 1889; *ibid.*, earlier literature; the same Zeitschr. 4, pp. 189 and 593, 1889; 6, p. 193, 1890; 8, p. 7, 1891; 9, pp. 266 and 386; and 10, p. 529, 1892; Küster, Zeit. phys. Chem. 5, p. 601, 1890, and 8, p. 577, 1891; Muthmann, Zeit. f. Krystall. 19, p. 357, 1891.

CRYSTAL MEASUREMENTS IN GENERAL.

When a chemist wishes to obtain measurements of a crystal he usually seeks the assistance of a crystallographer. In most chemical investigations the measurement of crystals is entirely omitted and the crystal form referred to only in a general way.

In fact, the more accurate goniometric and stauroscopic measurements require more practice than most chemists have had. On the other hand, it is advantageous for the chemist to be able to undertake, for simple crystal forms, the measurement of the most important angles (with a Wollaston goniometer), as well as the surface angle under the microscope, also the determination of the vibration planes, and even to make observations in convergent polarized light. These simpler measurements offer no great difficulty to a chemist who understands the principles of crystallography. These measurements become all the more necessary in recent times, owing to the importance of crystal form in the domain of stereochemistry, as well as for deciding problems of isomerism in general.

XVII. REFRACTIVE INDEX.

1. THE REFRACTOMETER OF ABBE.*

Principle, Method, and Apparatus (Fig. 70).—The light reflected from the mirror *g* passes through the glass parallelopiped *C*, which consists of a specially formed combination-prism (Fig. 71), into the cross-wire tube *J O*.

The telescope is fastened to the divided sector *A*, and the double prism *C* with the arm *B*, so that the position of the prism, with reference to the axis of the telescope, can be changed. The telescope can also be moved by means of the screw *K* and fastened in the desired position.

* Abbe, Apparatus for Determining Refraction, Jena, 1874, and Sitzungs-Berichte d. Jenaischen Gesellsch. f. Medic. u. Nat., Febr. 21, 1879.

If a liquid (or a suitable substance of smaller refractive index than the glass) is placed between the prisms, then the light which enters the prisms will, for a definite position of the prism, be totally reflected at the surface of the liquid and glass, and will no longer enter the telescope in parallel rays. The field of view of the telescope will then appear more or less darkened, depending upon the

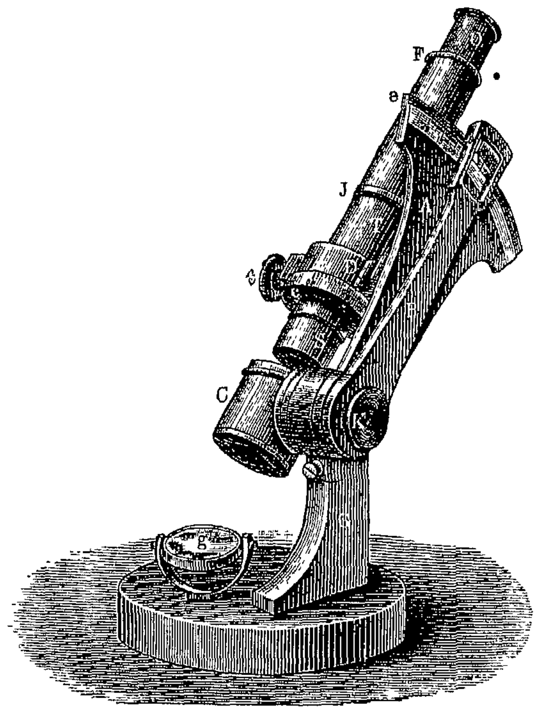

FIG 70.

position of the prism. For a definite adjustment of the prism one-half of the field of view will appear bright and the other half dark. For this position the refraction due to the liquid can be calculated from the angle of total reflection and the index of refraction of the prism by a simple formula.*

* *Loc. cit*, Abbe, Appaıatus, etc., p. 44.

To shorten the calculation, the divisions of the sector *A* are experimentally chosen, so that the index of refraction of the liquid for sodium light can be read off directly from the scale.

In many cases white light is employed. The fact that the different colors do not experience total reflection simultaneously must then be taken into account. The dividing line between the light and dark portions of the field of view appears colored for white light. This dispersion can be corrected by means of the compensator *D*.

This compensator consists of a direct-vision prism arrangement (p. 182), the two parts of which can be rotated in opposite directions by means of the screw *t*. The adjustment is so made that the rays of sodium light experience no divergence.* The influence of dispersion is eliminated for certain positions of the screw *t*, which are read off on the scale *c*. The dividing line between the dark and light portions of the field of view then appears sharp and uncolored. The scale *c* serves for the simultaneous measurement of the dispersion.

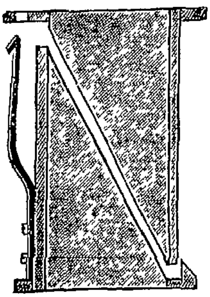

FIG. 71.

Method of Operation.—The apparatus is turned by means of the knob *K* until the sector at *e* comes in contact with the experiment-table. With the instrument in this position, the movable prism is carefully removed by pressing down the spring (Fig. 71); the prism surfaces are cleaned (with alcohol, water, etc.), and, after placing a narrow piece of thin paper on the short side, a drop of the liquid to be investigated is brought onto the hypothenuse-surface of the fastened prism.

The movable prism is then replaced and the telescope so adjusted that the arm *B* stands at the first division of the scale. The mirror is then turned toward the window or some artificial light, so that the whole field of view of the telescope appears light. The arm is then moved on the scale until the lower half of the field of view appears dark. Usually, a broad, colored border appears at the dividing line between the dark and light portions.

* Abbe, Apparatus, etc., *l. c.*, p. 50.

On turning the screw t, the colored border disappears, and the colorless dividing-line between the dark and light portions is then brought as sharply as possible onto the cross-wires by means of the arm B. The positions of the arm and compensator are read off; the screw t is then turned until the dividing-line at the middle of the cross-wires appears colorless a second time, the arm is readjusted, and the positions of the arm and compensator again read off.

The mean value of the two positions of the arm give directly the refractive index for the sodium line D. Inasmuch as the scale is graduated to thousandths for refractive indices, the results can be estimated, by means of a microscope, to the fourth decimal place.

The dispersion * between the Fraunhofer lines D and F can be calculated from the two positions of the compensator by means of a table which usually accompanies the apparatus.

Inasmuch as the refractive index n_D and the dispersion $n_F - n_D$ are known, the refractive index for any wave-length can easily be calculated from the Cauchy formula (p. 176). However, a knowledge of the refractive index for sodium light is usually sufficient.

The apparatus can also be used for determining the index of refraction of solids.

A thin, polished plate of the substance, together with a drop of a chemically indifferent, highly-refractive liquid, is placed between the prisms.

The following highly-refractive liquids are well adapted to these measurements: Oil of cassia ($n = 1.60$), cinnamic aldehyde ($n = 1.62$), sulphur chloride ($n = 1.654$), selenium chloride ($n = 1.653$), phenyl-sulphide ($n = 1.623$), phosphorus bromide ($n = 1.68$), monobrom-naphthalene ($n = 1.66$), and arsenic bromide ($n = 1.781$).

The index of refraction of the liquid compared with air is first accurately determined, then the refractive index of the liquid compared with the solid is determined in the manner described above. The first value divided by the second gives directly the index of refraction of the solid compared with air.

To test the accuracy of the instrument it is sufficient to make a series of observations with a substance of known refractive index,

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* Abbe, Apparatus, etc., pp. 48 and 75.

with white and also with sodium light. Any necessary correction should be applied to the readings on the scale.

The following are refractive indices for sodium light:

Water	at 20°	= 1.3329	(at 15°	= 1.3333)
Alcohol	"	= 1.3623	(sp. gr. 20°/4°	= 0.8000)
Acetone	"	= 1.3591	(" "	= 0.7920)
Ethylidene chloride	"	= 1.4165	(" "	= 1.1743)
Anilin	"	= 1.5863	(" "	= 1.0216)
Acetic acid	"	= 1.3718	(" "	= 1.0495)
Benzene	"	= 1.5863	(" "	= 0.8799)
Toluene	"	= 1 4955	(" "	= 0.8656)

For other refractive indices see, among others, Tabellen von Landolt-Börnstein, pp. 205–220, 1883, and Conrady, Zeit. phys. Chem. 3, p. 216, 1889; Die Brechungsindices des Wassers, Brühl, Ber. d. d. chem. Ges. 24, p. 644, 1891.

2. THE REFRACTOMETER OF PULFRICH.

Apparatus and Method in General.—A right-angled prism is placed in the upper part of a three-cornered support, fastened to the foot of the apparatus (Fig. 72). The horizontal and vertical surfaces of the prism form the above angle. The third inner prism stands inclined and is perfectly smooth.

The outer portion of the horizontal prism surface is slightly concave; it forms the base of a glass cylinder, which is fastened to the prism by means of cement. This cylinder is filled with the liquid to be investigated, and is provided with a small thermometer.

If the rays of light are brought together at the lower edge of the glass prism filled with liquid, by means of a lens fastened to the foot of the apparatus (not represented in the figure), then the light will pass from the liquid into the upper surface of the prism, and leave the prism through the vertical surface, provided the angle formed with the normal to the surface is less than the limiting angle of total reflection.

The telescope, provided with cross-wires and situated opposite the vertical prism surface (as shown in the figure), is fastened to a graduated circle with which it rotates. The beginning of the total reflection may be observed by adjusting the telescope so that the field of view appears dark in one portion and light in another.

The position of the telescope is determined, for which one-half of the field of view is light and the other half dark. The refractive index of the liquid can be calculated by a simple formula (p. 176) from the angle through which the divided circle rotates in passing from the zero of the scale to the required position.

Apparatus and Method in Detail.—The hollow, three-cornered support, in the upper part of which the prism is fastened, slides down over a three-cornered solid support, which is fastened to the foot of the apparatus.

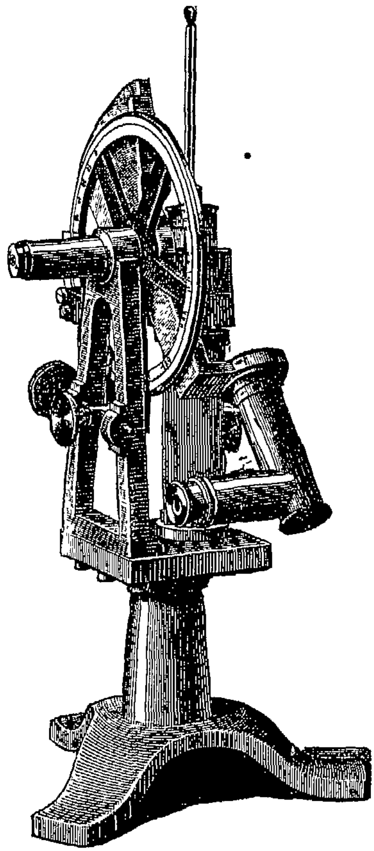

FIG. 72.

Inasmuch as the relative positions of the prism surfaces and the divided circle or telescope must always be the same, the inner and outer supports must be so constructed that the prism will remain constantly in its position.

The pressure-screw on the support should be tightened before each experiment; and care should be taken that, on removing the hollow support from the apparatus, no dirt or dust collects in the space between the outer and inner supports. The removal of the hollow support is, therefore, avoided as much as possible, and the glass cylinder which contains the liquid is usually cleaned by means of a pipet.

This cylinder is blackened on the side turned from the source of light, and is provided with a metallic cover, in the opening of which is placed a thermometer.

The cement on the cylinder (resin cement, gum arabic) must be frequently renewed. This must be done with the utmost care and cleanliness, as the rays of light enter the prism just above the cement.* If the liquid should ooze through the cement during the experiment, it should be removed by means of filter paper; the vertical surface of the prism should also be kept clean.

The telescope and divided circle are firmly fastened together. The telescope is adjusted for parallel rays of light, and is provided with cross-wires. The observer has only to focus the eye-piece sharply on the cross-wires, avoiding at the same time any rotation of the wires.

The zero point of the telescope is the horizontal position, which is fixed by the zero points of the divided circle and the vernier.

After the telescope has been approximately adjusted, the screw below the divided circle is firmly clamped, and the final adjustment made by means of the more delicate side-screw.

The circle is graduated to 0.5°. By means of the vernier, it is possible to read the scale to one minute.

Sodium light (sodium chloride, sodium bromide) is usually employed as the source of light. Thallium light and lithium light may also be used. The light should be as intense as possible, and should last for as long a period as possible. For contrivance see pages 185 and 207.

The prism which accompanies the instrument will answer for the investigation of most liquids. A prism of higher refractive index is necessary only for liquids whose refractive indices are greater than 1.6. Upon request, this extra prism will be furnished with the instrument.

Method of Operation.—The determination is carried out in an entirely or partially darkened room. The glass cylinder is filled with the liquid to be investigated and the screw on the support firmly tightened.

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* The glass cylinder in the more modern form of apparatus is provided around the interior of the lower end with a right-angled shoulder, which fits down over a corresponding shoulder on the prism-support The cement is placed only between the vertical portions of these shoulders, thus leaving the base of the cylinder where the light enters perfectly clear.

The source of light is placed at a distance of about ½ of a meter from the apparatus, so that the rays of light are brought together at the lower edge of the glass cylinder by means of the lens. When the adjustment is correct, a sharp, inverted image of the flame, in a darkened room, will be visible on a piece of white paper held in front of the cylinder. This image should be somewhat above the upper surface of the prism, toward the middle of the cylinder, as this is most suitable for the entrance of light into the prism.

When the observer is satisfied that the cemented portion is sufficiently tight and the glass surfaces clean, the telescope is so adjusted that the field of view is divided exactly in the middle, the upper portion being dark and the lower portion light. The angle through which the telescope has been turned from the zero point (horizontal position) is then read off on the divided circle (to one minute).

The index of refraction is calculated, according to page 176, from this angle i, which the last ray that enters the prism forms with the vertical surface of the prism on passing out.

The dividing line between the light and dark portions of the field of view should be as sharp as possible. If this is not the case, the intensity of the light is too low, or the position of the flame with reference to the apparatus is not properly adjusted, or the prism surfaces are not clean, or, lastly, the cementing has not been neatly done.

Enough liquid to cover the bottom of the cylinder is sufficient for the determination; the cylinder, however, must be carefully cleaned, either with the help of a pipette or by removing the support B (p. 173).

The temperature must be noted for each determination. In order to determine approximately the connection between the refractive index and the temperature, the liquid should be warmed before pouring into the cylinder; then, by repeated simultaneous observations of the temperature and refraction, the relation between the two can be established. See also page 178.

The time required for an observation amounts to only a few minutes. The different readings on the divided circle should not vary more than than 0.5 to one minute; this in general will give the refractive index accurate to within one unit in the fourth deci-

mal place, an accuracy which is sufficient for most chemical purposes.

To ascertain whether the instrument has undergone any change after long use, experiments are made with liquids of known refractive indices. See table, page 172.

It is better to carry out an experiment with water before each series of determinations.

Calculation of the Refractive Index n.—If i is the observed angle on the divided circle, and N the refractive index of the glass compared with air, then the index of refraction of the liquid compared with air is:

$$n = \sqrt{N^2 - \sin^2 i}.*$$

If the refractive index is to be reduced to the vacuum standard, n must be multiplied by the refractive index of air (at 0° and 760 mm.) = 1.00027. This reduction, however, is frequently omitted.

The values of N and n depend upon the wave-length of the light used in the experiment.

The values of N for the sodium, thallium, and lithium flames are:

	N
Na	= 1.61511
Tl	= 1.62043
Li	= 1.60949.

Sodium light is usually employed. As a matter of convenience, the refractive indices n, which correspond to the different values of i for sodium light, have been arranged in the form of a table (Sec. xxi). The results are given for angles which differ 10′ in magnitude; the intermediate values can easily be calculated by means of the differences d.

Sometimes it is necessary to calculate the refractive index of a substance for light of a definite wave-length to light of a different wave-length.

This calculation can usually be made very closely by means of the Cauchy formula †:

$$n_\lambda = A + \frac{B}{\lambda^2};$$

* For the development, see Ostwald, Lehrb. allgem. Chem., 2. Aufl., Bd. p. 406, 1891.

† Brühl, Zeit. phys. Chem. 1, p. 308, 1887.

n is the refractive index for light of wave-length λ; A and B are two constants, the values of which can be determined if the refractive indices n_1 and n_2 for the wave-lengths λ_1 and λ_2 are known. The formulas are:

$$A = \frac{n_1\lambda_1^2 - n_2\lambda_2^2}{\lambda_1^2 - \lambda_2^2}$$

and

$$B = (n_1 - A)\,\lambda_1^2.$$

If the values thus obtained for A and B are substituted in the equation

$$n_\lambda = A + \frac{B}{\lambda^2},$$

the refractive index n_λ can be calculated for any light of known wave-length.

The wave-lengths λ (in millionths of a millimeter) for the different kinds of light usually employed are:

	λ
Potassium (red line)	= 768.0
Sodium (yellow line)	= 589.3
Lithium (red line)	= 670.8
Thallium (green line)	= 534.9
Hydrogen (red line) H_α	= 656.3
Hydrogen (green line) H_β	= 486.1
Hydrogen (violet line) H_γ	= 434.0.

Choice of Method for Determining the Refractive Index.—The apparatus of Abbe or Pulfrich is usually employed for chemical purposes. These methods are both accurate to from one to two units in the fourth decimal place. Both methods are extremely simple; especially the method of Abbe, owing to the small quantity of liquid required.

The uncertainty of the temperature is an objection to the method of Abbe. The method of Pulfrich has the disadvantage that the cylinder must be frequently cemented to the prism.

If the refractive index is to be determined accurately to the fifth decimal place, a good spectrometer, with horizontal divided-circle, must be employed. Wiedemann and Ebert, Physik. Prakt., p. 255, 1890; Kohlrausch, Prakt. Phys. VII, p. 146, 1892; Glazebrook and Shaw, Physik. Prakt., Leipzig, p. 287, 1891.

Determination of refractive indices at higher temperatures, Brühl, Ber. d. d. chem. Ges. 24, p. 286, 1891.

Specific Refraction, Atomic and Molecular Refraction.—The determination of the refractive index and its relation to temperature is not of itself sufficient for chemical problems. There are definite relations between the refractive index n and the density d determined at the same temperature. These relations are independent of the temperature. Such relations which are of importance in the development of chemical laws are shown by the expressions:

$$\frac{n-1}{d} \quad \text{and} \quad \frac{n^2-1}{n^2+2}\,\frac{1}{d}.$$

These expressions are known as the "specific refraction," or simply the "refraction constant." The second Lorentz-Lorenz n^2 formula, for practical and theoretical reasons,* is used almost exclusively.

The refraction constant is further multiplied by the atomic or molecular weight, for the development of stochiometric laws.

The expression

$$\frac{n^2-1}{n^2+2}\,\frac{a}{d}$$

is called the atomic refraction, and the expression

$$\frac{n^2-1}{n^2+2}\,\frac{m}{d}$$

the molecular refraction.

For the calculations, see Table of Atomic Weights, page 229, and also the table on page 235, which gives

$$\log \frac{n^2-1}{n^2+2}$$

for the different values of n. The molecular refraction is calculated to the second decimal place.

* Brühl, Ber. d d. chem. Ges. 19, p. 2746, 1886; Liebig's Ann. 235, p. 1, 1886; and Zeit. phys Chem. 1, p. 310, 1887; 7, p. 1, 1891; Weegmann, Zeit. phys. Chem. 2, pp. 219 and 258, 1888; Schütt, *ibid.* 5, p. 348, 1890.

APPLICATION OF REFRACTIVE INDICES TO CHEMICAL PROBLEMS.

1. The refractive index may be used to determine the degree of purity of a substance; it is also frequently used in technical work for the identification of substances.

For tables of refractive indices see, among others, Landolt-Börnstein, Phys. chem. Tab., pp. 204–220, 1883; Kanonnikoff, Jour. pr. Chem. [2] 32, p. 497, 1885; Brühl, Zeit. phys. Chem. 1. p. 312, 1887; 7, pp. 25 and 159, 1891; Jahn, Wied. Ann. 43, p. 280, 1891; Conrady, Zeit. phys. Chem. 3, pp. 216 and 223, 1889.

2. The refractive index can often be advantageously employed to determine the concentration of a solution or mixture.

If 100 parts of a mixture of a solution contain p parts of the one, and therefore $100 - p$ parts of the other constituent, and n and d represent the refractive index and density of the mixture (solution), n_1, n_2, and d_1, d_2 the corresponding values for the two constituents of the mixture, we have the following equations:

$$\frac{n-1}{d}\,100 = \frac{n_1 - 1}{d_1}p + \frac{n_2 - 1}{d_2}(100 - p)$$

and

$$\frac{n^2-1}{n^2+2}\,\frac{100}{d} = \frac{n_1^2-1}{n_1^2+2}\,\frac{p}{d_1} + \frac{n_2^2-1}{n_2^2+2}\,\frac{100-p}{d^2}.$$

If, therefore, the refractive indices for a number of concentrations are known, or if the refraction constants of a solution and those of its constituents are known, then the concentration can be approximately determined from one of these two formulas. On the other hand, the refraction constant of a liquid or solid can be approximately calculated from the refraction values of their solutions or mixtures of known concentrations. As to the degree of accuracy, see the work of Schütt, Zeit. phys. Chem. 5, p. 349, 1890, and 9, p. 349, 1892, and the bibliography in the same Zeitschr. 5, p. 349.

3. The refraction constants (atomic and molecular refractions) are of considerable value in the determination of the constitution of organic compounds.

The molecular refraction of a compound is equal to the sum of its atomic refractions. *

If m is the molecular weight of a substance, the molecule of which consists of p, q, r . . ., atoms of the elements whose atomic weights are a_1, a_2, a_3 . . ., and n and d are the refractive index and density of the substance, and n_1, n_2, n_3 . . . and d_1, d_2, d_3 . . . the corresponding values for the elementary atoms contained in the body, then

$$\frac{n^2 - 1}{n^2 + 2}\frac{m}{d} = p\,\frac{n_1{}^2 - 1}{n_1{}^2 + 2}\frac{a_1}{d_1} + q\,\frac{n_2{}^2 - 1}{n_2{}^2 + 2}\frac{a_2}{d_2} + r\,\frac{n_3{}^2 - 1}{n_3{}^2 + 2}\frac{a_3}{d_3} + \ldots$$

The atomic refractions of most elements are known. The molecular refraction of a compound, then, can be (1) determined directly; (2) calculated from the sum of the atomic refractions. The observed and calculated values should agree. This is usually, but not always, the case. Frequently the influence of the constitution of the compound must be taken into account.

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* The Landolt-Brühl theory may be formulated as follows:

1. Position isomerides have equal specific and molecular refractions; saturation isomerides have different refraction constants

2. Polymers never show equal specific refractions nor multiple molecular refractions corresponding to the molecular weights.

3. A change of complex atomic groups to simpler groups is always accompanied by a decrease in the refraction.

4. The optical effect of building up a more complex substance is the same, whether an open-chain compound (amylene, diamylene) or a closed-ring compound (paraldehyde, cymhydrene, menthol, etc.) or compounds with several rings (pinene, cyneol) result.

5. The molecular refraction of truly saturated bodies is approximately equal to the sum of the atomic refraction calculated from the empirical formula. All those compounds which exhibit only single-linking of atoms may be considered saturated; these represent the true paraffins or derivatives of the general formula $(C_nH_{2n+2}) - xH_2$.

6. All unsaturated compounds show a refractive increment which is approximately proportional to the number of ethylene, acetylene, or carbonyl groupings. The less the dispersive power of the substance, the more nearly this proportionality holds true.

See Brühl, Zeit. phys. Chem. 1, p 340, 1887, and *ibid.* 7, p. 189, 1891, and Weegmann, *ibid.* 2, pp. 222 and 369, 1888. On the influence of dispersion, see Brühl, Liebig's Ann. 235, 1, and Ber. d. d. chem. Ges. 19, p. 2746, 1886.

If a compound containing C, H, O is investigated, then the influence of the single, double, and triple linking of carbon atoms on the refraction must be taken into account. The sum of the atomic refractions must be increased by a "refraction increment" $= 1.7$ units (for sodium light) for each double bond between two carbon atoms. The atomic refraction of carbon, when singly linked to oxygen, is also different from that when it is doubly linked, and these values are less than for carbon atoms bound together with one or two bonds. (See table below.)

If, therefore, the molecular refraction calculated on the assumption of single linkings is less than the observed value, it indicates, when the manner in which the oxygen is linked does not come into consideration, the presence of double bonds between carbon atoms. The number of double bonds may be found by dividing the difference between the observed and calculated values by 1.7.

The following table contains some of the most important atomic refractions, calculated from the n^2 formula of Conrady,* Brühl,† and Landolt for sodium light and the C-line of hydrogen.

$\vDash$ represents the double linking; $|\!\equiv$ the triple of carbon; C′ represents a carbon atom in the middle of a chain of carbon atoms; C° a single carbon atom; O′ hydroxyl-oxygen; O″ carbonyl-oxygen; O^2 ether-oxygen; and N′ a nitrogen atom singly linked to carbon.

	Atomic Weight.	Atomic Refraction for Sodium Light.	Approximate Atomic Weight.	Atomic Refraction for Sodium Light.	Atomic Refraction for the C-line.	
				Conrady.	Landolt.	Brühl.
$\vDash$	. . .	1.707	. . .	1.707	1.78	1.836
$\vert\!\equiv$	. . .	. . .	. . .	. . .	. . .	2.22
C′	11.97	2.494	12	2.501	2.48	2.365
C°	11.97	2.586	12	2.592	2.48	. .
H	1	1.051	1	1.051	1.04	1.103
O′	15.96	1.517	16	1.521	1.58	1.506
O″	15.96	2.281	16	2.287	2.34	2.328
O^2	15.96	1.679	16	1.683	1.58	1.655
N′	. . .	. . .	14	. . .	. . .	2.76
Cl	35.37	5.976	35.5	5.998	6.02	6.014
Br	79.76	8.900	80	8.927	8.95	8.863
I	126.54	14 12	126.5	14.12	13.99	13.808

* Conrady, Zeitschr. phys. Chem. 3, p. 226, 1889. † Brühl, *ibid.* 7, p. 191, 1891.

The difference between certain of these values is rather small. C′ and C° differ very slightly, the difference between O′ and O^2 being somewhat larger.

On the relations for nitrogen, see Löwenherz, Zeit phys. Chem. 6, p 552, 1890; Brühl, Zeit. phys Chem. 7, p. 176, 1891, and Ber d. d. chem. Ges. 26, p. 806, 1893; Trapesonzjanz, Ber. d. d. chem. Ges. 26, p. 1428, 1893; for sulphur: E. Wiedemann, Wied Ann. 17, p. 577, 1882; Nasini, Gazz. Chim. Ital. 13, p. 296, 1883, and Rend. Lincei 2, p. 623, 1886; 6, pp. 259 and 284, 1890; Nasini and Costa, Veröffentl. chem. Instit. Rom, Ref. Zeit. phys. Chem. 9, p. 639, 1892

On the relation of refraction to the constitution of compounds, influence of the double bond, etc, see Brühl, Ber. d. d. chem. Ges 12, p. 2135, 1879, and 19, p. 3103, 1886; Liebig's Ann. 200, p. 139, 1880; Zeit. phys. Chem. 1, p. 311, 1887; Wallach, Liebig's Ann. 245, p. 191, 1888.

Kanonnikoff, Jour. pr. Chem. (2) 32, p. 497, 1885; Weegmann, Zeit. phys. Chem. 2, p. 229, 1888; Landolt and Jahn, molecular refraction and dielectric constant, Zeit. phys. Chem. 10, p. 289, 1892; refraction of gases, Brühl, Zeit. phys Chem. 7, p 1, 1891.

Determination of dispersion: Brühl, Zeit. phys. Chem. 1, p. 357, 1887, and 7, p. 140, 1891, *ibid.* literature; Nasini, Roma. Accad. d. Lincei Rendiconti febbrajo, 1887; Weegmann, Zeit. phys. Chem. 2, p. 235, 1888; Barbier and Roux, Compt. rend. 112, p. 582, 1891; Gladstone, Jour. Chem Soc. 59, pp. 290 and 589, 1891.

XVIII. SPECTRUM ANALYSIS.*

1. THE DIRECT-VISION SPECTROSCOPE.

Many elements and compounds which give characteristic emission or absorption spectra may be recognized by means of the small apparatus represented in figure 73.

Two brass tubes, movable one in the other, contain a combination of crown and flint-glass prisms which cause the dispersion of

* For the theoretical consideration of spectrum phenomena see, among others, Kayser, Lehrbuch der Spectralanalyse, and H. W. Vogel, Praktische Spectralanalyse.

the light that passes through. The rays of light enter through the slit *s*, and pass through the lens *c* and the prism combination into the eye-piece *o*.

FIG. 73.

The instrument is adjusted by means of the sun spectrum. The inner tube is moved to such a position in the outer tube that the Fraunhofer lines of the sun spectrum appear sharp.

2. THE SPECTROSCOPE OF BUNSEN.

Apparatus (Fig. 74).—This consists, in its essential parts, of a collimator *A*, through which the light enters, the observing-tube *B*, the scale-tube *C*, and the prism *P*.

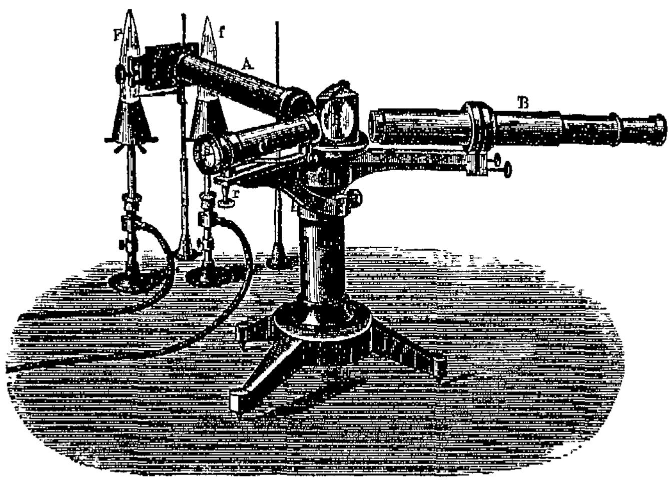

FIG. 74.

The collimator is so adjusted that the rays of light which enter the slit in the plate *f* fall parallel on the prism *P*, by means of which they are dispersed; the image of the spectrum is formed in the telescope *B*.

The image of the micrometer scale in the tube *C* is also visible just above the image of the spectrum. By means of this the relative positions of the different portions of the spectrum can be determined.

Adjustment of the Apparatus.—It is, above all, necessary that the rays of light leave the collimator in a parallel direction, and that the image of the slit appears distinct in the telescope. To accomplish this the eye-piece of the telescope is adjusted so that the cross-wires appear sharp. The telescope is then removed from its support and focused sharply on some distant object (church steeple, tree, etc.). By means of a mark this adjustment of the telescope for parallel rays is fixed once for all.

The prism is then removed and the telescope placed directly opposite the collimator *A*. The slit is illuminated and its position adjusted so that the slit and cross-wires appear sharp at the same time, and so that no parallax is produced on moving the eye. By raising or lowering the telescope the middle of the slit can be made to coincide with the middle of the cross-wires.

If the prism has not already been adjusted to the position of minimum deviation, it may be so adjusted in the following manner:

The slit is illuminated with sodium light, the prism is given a chance position, the direction of the outgoing rays determined by means of the naked eye, and the telescope turned so that the sodium line coincides with the cross-wire. The prism is then turned in the direction of the refracting edge, the telescope being moved at the same time. This rotation is continued until the image of the slit begins to move in the opposite direction. This position of the prism, for which the change in direction begins, is the position of minimum deviation. The prism should be fixed in this position.

Finally, it is necessary that the image of the scale should be distinct in the telescope.

The scale-tube is illuminated by means of a small flame, which should not be placed too near the tube, and given such a position that the image of the scale is visible above the spectrum. The scale-tube is then drawn out until the scale divisions appear sharp in the telescope, and so that the image of the scale produces no parallax with the image of the slit on moving the eye. The hori-

zontal position of the scale is brought about by rotating the scale-tube.

Reduction of Scale Values to Wave-lengths.—It is especially desirable, for scientific purposes,* that the positions of the different portions of the observed spectrum be expressed not in terms of an arbitrary scale, but in wave-lengths of the light employed.

The scale-tube is given such a position that the division 100 coincides with the middle of the sodium lines. This coincidence is preserved in all the movements of the telescope. The reduction of the scale values to wave-lengths is accomplished then by means of elementary spectra or the sun spectrum.

In the first case a series of salts, which show characteristic lines of known wave-lengths throughout the whole range of the spectrum,

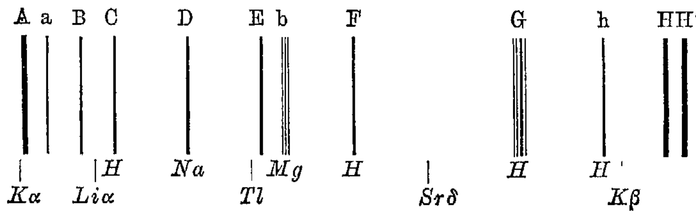

FIG. 75.

are vaporized in the Bunsen burner which illuminates the slit. The following lines, whose positions in the spectrum are shown in figure 75, are especially adapted to this purpose:

				Wave-lengths in Millionths of a Millimeter ($\lambda . 10^{-6}$).
Potassium	red	line	K_α	768
"	blue	"	K_β	404.6
Lithium	red	"	Li_α	670.8
Sodium	yellow	"	Na	589.0–589.6
Thallium	green	"	Tl	534.9
Strontium	blue	"	Sr_δ	460.8

As a matter of convenience for introducing the substances into the flame, the molten chlorides of the metals may be fastened, in

* For technical purposes, identification of colors, determination of concentrations, etc., this calculation to wave-lengths is unnecessary.

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the form of beads, on platinum wires and a number of such wires arranged in a horizontal position, movable around a vertical axis; or, still better, a spoon of platinum gauze (p. 205) may be employed. See also the arrangements of Pringsheim, Wied. Ann. 45, p. 426, 1892, and Kayser, Lehrb. d. Spektralanalyse, p. 77, 1883.

If an exhausted Geissler tube be partially filled with hydrogen and the electric spark (small induction coil with three chromic-acid elements) passed through the tube, the four hydrogen lines H_α, H_β, H_γ, and H_δ ($\lambda = 656.3$, 486.1, 434.0, and 410.2), corresponding to the Fraunhofer lines C, F, G, h (Fig. 75), are visible and may be used for reducing the scale divisions to wave-lengths. The accuracy of this reduction to wave-lengths depends upon the number of lines observed * and their distribution in the different portions of the spectrum.

When the scale divisions corresponding to a number of lines have been once determined, the relation of the same to the wave-lengths is represented graphically.

The scale divisions are laid off as abscissas, and the wave-lengths as ordinates, on millimeter paper. It is possible, then, by means of the curve which is determined by these points, to represent the position of any line in wave-lengths.

A greater accuracy may be obtained by means of the sun spectrum.

The slit is illuminated by direct sunlight or bright clouds, and then, according to the accuracy desired, the positions of 10, 20, or 50 characteristic Fraunhofer lines are determined. A number of the most important of these lines are shown in figure 75. The wave-lengths of the lines, which are not given in the previous page, are as follows:

		$\lambda \cdot 10^{-6}$			$\lambda \cdot 10^{-6}$
Line	A	760.4	Line	C	517.3
"	a	718.6	"	H_1	396.6
"	D	687.0	"	H_2	393.4
"	E	527.0			

When a larger number of Fraunhofer lines are observed, reference may be made to Angström's Tables; or to Kayser's Lehrbuch

* Landolt-Börnstein, Tables of Spectrum Lines, pp. 200–203, 1883.

über Spektralanalyse; likewise to that of G. and H. Krüss, Kalorimetrie und quantitative Spektralanalyse.

Special Rules for Spectrum Observations. Emission and Absorption Spectra.—The chlorides are usually employed to obtain metallic spectra. These are volatilized on a platinum wire in the outer portion of the Bunsen flame; difficultly volatile oxides should be moistened with hydrochloric acid.

The observer must not be deceived by the sodium lines which are always visible, or the faint green and blue lines which are due to the lower part of the Bunsen flame.

For observations of very faint lines, the flame which illuminates the scale should be removed until the cross-wire has been adjusted to the desired line; the scale is then illuminated and the position of the cross-wire determined.

It is also necessary that all foreign light be excluded during the observations. The prism and the objectives of the three tubes are therefore covered with a black cloth; a screen of black paper is also placed around the eye-piece of the telescope, to protect the eye from the illuminating flame.

The spectroscope is usually provided with a comparison prism, by means of which the lower half of the slit can be covered. By this arrangement it is possible to determine the identity of substances without accurate measurements.

Direct light is allowed to enter the upper half of the slit, while light from a flame placed to one side (Fig. 74), through total reflection, enters the lower half of the slit. The substance to be investigated is introduced into one flame, and the comparison substance into the other. The two spectra will appear one above the other, and in case of identity of the two substances the lines of the one spectrum must be the prolongations of the lines of the other.

For qualitative observations of the absorption spectra of colored solutions, the solution to be investigated should be placed in a glass prism with parallel sides (Fig. 80, p. 195), between the flame (petroleum flame) and the slit-tube. Inasmuch as the absorption spectra depend upon the concentration of the solution, the observations are extended to solutions of different concentrations, dilute and concentrated. The temperature and the nature of the

solvent also influence the absorption. The spectroscope should be placed in a room of almost constant temperature (about 18°); then the influence of temperature for all observations within the temperature-interval 15 to 21° can be neglected.*

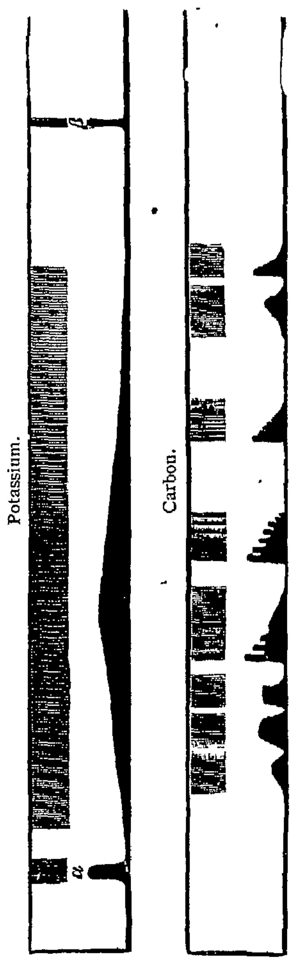

FIG. 76.

The positions of maximum darkness, for an absorbing substance, are the most important absorption bands.

The positions, in wave-lengths, of the edges of the absorption bands are determined for solutions of different concentrations. The greater the dilution, the narrower the bands, and the more nearly do they coincide for different solutions. If the darkness of the observed bands increases symmetrically about the middle position, then the arithmetic mean of the band edges for very dilute solutions represents approximately the position of maximum darkness. This position, then, from observations on extremely dilute solutions, can be interpolated.† The determination of the position of maximum darkness is especially desirable for the identification of substances.

Spectrum investigations in general depend not only upon the positions of the lines and bands, but also on their distinctness and dimensions; a sketch—or better, photograph—should therefore be made of the observed spectrum.

* Bremer, Zeit. anorg. Chem. 1, p 112, 1892.

† Krüss, Zeit. phys. Chem. 2, p. 314, 1888.

The sketch may be prepared as shown in figure 76. The lines and bands are represented by black lines and shadings of equal length. The intensity of the spectrum lines may be indicated by the intensity of the lines in the sketch; or, better, by the curve in the same line where abscissas correspond to scale divisions or wave-lengths and the ordinates to intensities.

On the application of photography to spectrum analysis, see Ostwald, Zeit. phys. Chem. 9, p. 582, 1892.

3. THE UNIVERSAL SPECTROSCOPE OF KRÜSS.*

This instrument is a modification of the Bunsen-Kirchhoff apparatus, and consists, as does the ordinary apparatus, of the prism, a collimator with comparison-prism, a scale-tube, and the observing telescope (*A*, *B*, and *C*, Fig. 77).

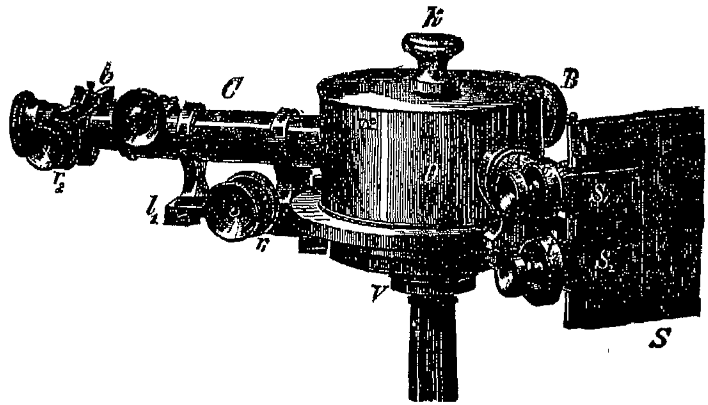

FIG. 77.

The advantages in the construction of this apparatus are:

1. The different parts of the apparatus have been adjusted as far as possible by the manufacturer.

2. The measuring contrivance is especially accurate.

3. The instrument is provided with an arrangement on the slit-

* Reference: A. Krüss, in Hamburg.

tube for quantitative measurements according to the method of Vierordt.

The collimator *A* can not be adjusted; the manufacturer has taken special care that the slit stands exactly in the focus of the objective and parallel to the refracting edge of the prism. The single slit is generally used, the double slit being attached only for the method of Vierordt (p. 193).

The sides of the slit are made of platinum, and the width of the opening can be regulated and determined by means of a micrometer screw. The slit should be narrowed until the spectrum image is as sharp as possible. If the platinum edges of the slit are not clean, then the spectrum will contain horizontal streaks. In such cases the edges should be cleaned by drawing a piece of glazed paper through the almost closed slit.

The scale-tube *B* is also free from adjustment. The scale is placed in the focus of the objective, and the tube fixed so that the middle of the sodium line * coincides with the scale division 100. For all measurements where extreme accuracy is not required, the scale may be used and the contrivance on the observing telescope neglected. The scale divisions are reduced to wave-lengths, as described on page 185.

The observing telescope *C* is provided with cross-wires. The telescope and cross-wires are adjusted by means of the special contrivance represented in figure 78, which is used instead of the scale for fine measurements, especially for carrying out the method of Vierordt.

The telescope is turned about its vertical axis by means of the screw and measuring contrivance $r_1\, l_1\, i_1$, situated directly below the eye-piece *o*. The micrometer screw is provided with a graduated head r_1 (100 divisions); the number of whole rotations can be read directly from the contrivance $l_1\, i_1$.

After adjusting the cross-wires, then, to a definite place in the spectrum, it is possible to represent the relative positions in the spectrum to four places. The first two are expressed by the divisions on the index $l_1\, i_1$, and the others by the screw-head r_1.

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* The sodium line *D*, as is known, consists of two lines, visible when the slit is very narrow.

Inasmuch as the cross-wires can be moved by means of the micrometer screw $l_2 r_2$, it is necessary, before using the contrivance $l_1 r_1$, to place $l_2 r_2$ on the zero.

This second micrometer screw, with the contrivance $l_2 r_2$ for moving the cross-wires, is used for fine measurements in the spectrum.

From the known relation between the value of these two micrometer screws, the results obtained by either contrivance can be calculated into terms of the other, likewise into scale divisions, so

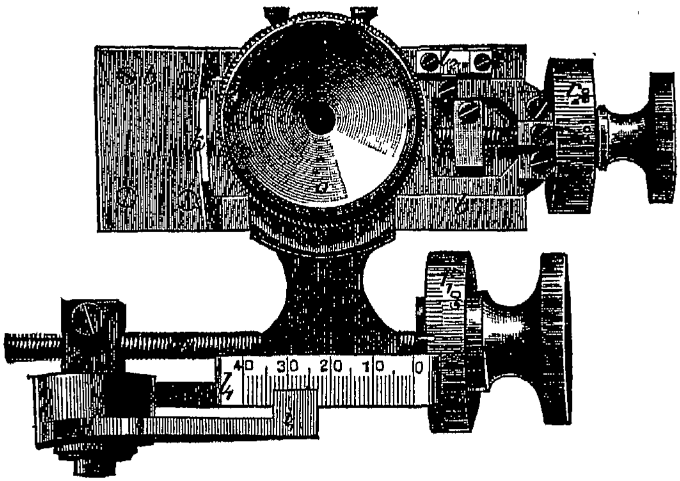

FIG. 78.

that it is possible to make control-measurements by three independent methods.

The contrivance $r_2 l_2$ has still a special use. The cross-wires move in the slide *b* through an opening in the eye-piece; this slide lies in the focal plane of the eye-piece, and is provided with the slit *k*, which, for observing faint lines and for carrying out the method of Vierordt, is used to screen the portions of the spectrum not in use.

In case the positions in the spectrum are determined by moving $l_1 r_1$, then $l_2 r_2$, as already mentioned, must be adjusted to 0. The cross-wires for this adjustment are in the middle of the field of

view, provided the contrivance has first been shoved from right to left as far as possible into the eye-piece. For this adjustment of the instrument, $l_2 r_2$ on o and the cross-wires in the middle of the field of view, the slit k is closed. If the slide is then shoved from left to right in the eye-piece, until the movement is again stopped by means of a special contrivance on the instrument, the field of view will be dark, owing to the spectrum being covered by the closed slit, and the line of contact of the two sides of the slit will coincide with the middle of the cross-wire. If the slit is unsymmetric, as in the older form of apparatus, then, on opening to a definite width by moving $l_2 r_2$, the left side remains stationary and the width of the slit or the spectrum region can be read off directly from the measuring contrivance $r_2 l_2$.

In the more recent form of apparatus the slit opens symmetrically on the two sides, and the light from the two edges of the spectrum region has a mean wave-length, which was established in the previous adjustment of the cross-wires by moving $l_1 r_1$, while the width of spectrum field is determined by means of $l_2 r_2$.

The divisions on $r_1 l_1$ and $r_2 l_2$ are reduced to wave-lengths according to the method on page 185. The positions of 20 to 30 Fraunhofer lines should be determined for this purpose. The spectrum region is then represented in wave-lengths (*e. g.*, $\lambda\, 612.7 - \lambda\, 604.3$).

The universal spectroscope is provided with two prisms: 1. A single flint-glass prism, with a refracting angle of 60° and a mean dispersion of $A - H_2 = 4° \; 30'$; 2. a Rutherford prism, with a dispersion of $A - H_2 = 8\text{–}11°$.

On account of the greater intensity of the spectrum, the first prism should always be used for ordinary qualitative investigations and where the determinations are to be made as quickly as possible. The Rutherford prism is placed in the instrument only when it is necessary to widen the range of the spectrum and attain the greatest accuracy possible in the measurements.

The prisms are placed in a closed, light-proof cap D (Fig. 77), and are held in the position of minimum deviation by the pressure of a spring fastened to the lower side of the knob K. By means of a simple contrivance the prisms can be automatically adjusted to the position of minimum deviation for any movement of the observing telescope.

4. THE UNIVERSAL SPECTROSCOPE AS SPECTROPHOTOMETER.

METHOD OF VIERORDT.*

Principle and Calculation.—The object of the photometric measurements is to determine the amount of absorption for a definite range of the spectrum when the light is passed through an absorbing medium. These measurements are especially valuable in the investigation of liquids (solutions).

The method of Vierordt depends upon the use of a double slit, which can be fastened on the collimator of a spectroscope instead of the single slit.

The intensity of a definite kind of light is proportional to the width of the slit. If, therefore, the spectroscope is provided with two slits, one directly above the other, either of which can be adjusted independently of the other, then two spectra in contact will be formed, the intensities of which will be different, provided the slits are of equal width and illuminated by lights of different intensities. If, however, the widths of the slits are so adjusted that the two spectra for any definite range are of equal intensities, then the intensities of the two lights are proportional to the widths of the slits. If the intensity of one light be placed = 1, the intensity of the other is obtained from the relative widths of the two slits, which can easily be determined.

The absorption of light by a layer of liquid depends upon the thickness of the layer. The results are referred, therefore, to a layer of liquid 1 cm. in thickness.

The operation is usually carried out so that the light which enters one slit has passed through a layer of the given liquid 1 mm. in thickness, while the light from the same source, which enters the other slit has passed through a layer of the same liquid 11 mm. in thickness. If the slits be then adjusted so that the two resulting spectra are of the same intensity, and the intensity of the original light be placed = 1, then the ratio of the widths of the two slits

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* Vierordt, Use of the Spectroscope for Photometry in Absorption Spectra, Tübingen, 1873.

gives directly the intensity J' of the light after passing through a layer of the liquid 1 cm. in thickness.

The extinction-coefficient e is calculated from the value of J', and may be defined as the reciprocal value of the thickness which a substance must have in order to decrease the intensity of the light which passes through it to $\frac{1}{10}$ of the original intensity. e and J' bear to each other the simple relation that $e = -\log. J'$. For the development of this relation, see Krüss, Kolorimetrie und Spektralanalyse, p. 78, 1892, and Methoden der Analyse, p. 84, 1892. The abbreviated table of Vierordt for the calculation of e from J' is given on page 233.

In the case of solutions the extinction-coefficient depends upon the concentration c, where c represents the number of grams of dissolved substance in 1 c.c. of solution. So nearly is this coefficient proportional to the concentration that the quotient $\frac{c}{e} = A$; *i. e.*, the absorption ratio for each dissolved substance may be regarded as constant.

In general, the intensity J', the extinction-coefficient e, and the absorption-ratio A should be determined in different portions of the spectrum for each concentration of solution.

Apparatus and Method of Operation.—The universal spectroscope may be used advantageously.

The single slit is replaced by a double slit (Fig. 79); *i. e.*, one slit divided into two halves by means of a horizontal contrivance, so that each half can be adjusted independently of the other by means of the two fine measuring screws t_1 and t_2. To obtain good results it is necessary that the slits should open symmetrically on both sides.*

The width of the slit is read off in terms of the scale divisions on the head of the measuring screw. Each rotation of the screw corresponds to 100 divisions. The width of one slit is placed = 1, corresponding to 100 scale divisions. To produce the same intensity of light for a definite color, the other slit must be 30 scale divisions in width; then 0.3 represents the intensity J', from which the extinction-coefficient e may be obtained directly from the table (p. 229).

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* Krüss, Kolorimetrie und Spektralanalyse I, p. 86, 1892.

The liquid to be investigated is placed in a vessel of the form represented in figure 80,—a glass vessel with parallel sides, and 11 mm. in thickness. The vessel is provided with the Schulz

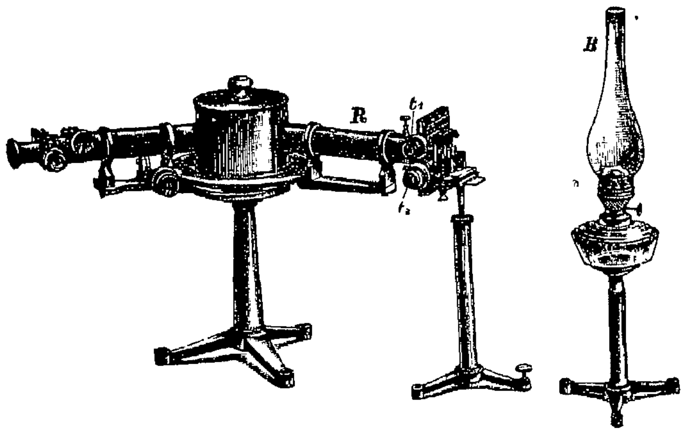

FIG. 79.

glass body *a*, a rectangular glass prism 10 mm. in thickness. The light, therefore, must pass through a layer of liquid 1 or 11 mm. in thickness. In the observation the intensity of the light which passes through a layer of the liquid 1 cm. in thickness is compared with the intensity of the same light when passed through the prism *a* into the lower slit. If the upper slit is adjusted to 100 divisions in width, and the lower slit adjusted so that the lights are of equal intensities, then the value of J' can be read off directly from the lower screw-head.

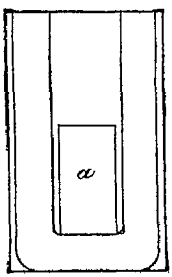

FIG. 80.

The liquid in the glass vessel must be free from air-bubbles; these can be removed by means of a platinum wire. In case a very volatile solvent is used, a vessel which can be closed must be used to contain the liquid.

The vessel containing the liquid is placed on a suitable stand directly in front of the slit (Fig. 79). The apparatus is illuminated by means of an electric light, the Auer light, or a petroleum lamp *B*, as shown in the figure.

The lamp is placed directly in line with the collimator *R*, about 10 cm. from the vessel containing the liquid; the broad surface of the flame should be parallel to the direction of the collimator. The two halves of the slit must be equally illuminated by the flame. The middle of the flame, therefore, must be of the same height as the dividing line between the two halves of the slit. To determine when this condition is fulfilled the one slit is opened 30 divisions and the other adjusted so that the intensities of the corresponding spectrum regions are the same.* If the lamp is properly adjusted, then the second slit must be of the same width (= 30 divisions) as the first.

It is further necessary, when the opening of the slit is closed slowly, that the graduated screw-head should stand at 0 the instant at which all the light is extinguished. If this is not the case, the screw-head and vernier must be adjusted to this condition.

The vessel containing the liquid must be placed directly in front of the slit, so that the upper surface of the glass prism is horizontal and in the same plane with the line dividing the two halves of the slit. If this condition is not fulfilled, a broad, shadowy band appears in the spectrum, the width of which must be reduced to a rather heavy line by adjusting the foot-screws of the stand so that the upper surface of the prism is horizontal. This line is finally brought into coincidence with the dividing line of the two slits, which is made visible by opening the slits to different widths. This adjustment is made by regulating the height of the horizontal surface of the prism by means of the broad screw contrivance on the stand. See page 198 on the use of the Hüfner-Albrecht rhomb. The scale attached to the observing telescope (p. 191) is used to determine the exact wave-lengths of the spectrum region investigated; and the limits of a definite spectrum region are determined by means of the eye-piece slide described on page 191.

To obtain accurate results, the method should be carried out in that portion of the absorption spectrum where there is no sudden change of intensity, but where the intensity increases or decreases gradually. There is less liability to error when the slit in the eye-

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* The adjustment of the two slits to equal illuminations should be made several times. This can be more easily accomplished in the green portion of the spectrum.

piece is as narrow as possible; the minimum width, however, should not be less than 50 divisions on the micrometer screw.

Other conditions must also be observed in observations on solutions:

1. The solution must be approximately at the temperature of the room; in regard to the influence of temperature on the constant of the apparatus, see page 188. A temperature difference of 4 to 5° may be neglected. Care must be taken that the heat from the source of light does not produce a greater variation than 5° (Bremer, Zeit. anorg. Chem. 1, p. 112, 1892).

2. The influence of the solvent on the value of J', owing to the absorption and reflection of light, must not be neglected.

If the glass vessel is filled with water, the upper slit must be adjusted to a width of 90.5 divisions on the micrometer, while the lower slit is 100 divisions in width, in order that the two intensities shall be equal. In the investigation of all aqueous solutions, then, the upper micrometer must be placed on 90.5, and the lower on 100, for the starting point of the measurement.

According to Krüss, if the lower micrometer is adjusted to 100, the upper one, for various solvents, should be adjusted as follows:

For alcohol (90 per cent.)	=	95.0
For alcohol absolute	=	110.0
For ether aqueous	=	98.0
For ether anhydrous	=	91.5
For chloroform anhydrous	=	112.0
For benzene anhydrous	=	102.5
For glacial acetic acid anhydrous	=	88.0

The measurements were made within the spectrum region: λ 513.1 — λ 523.0. It is desirable, however, that the amount of absorption be determined for each solvent, for the values may vary from those given above.

3. It is also necessary to determine the most suitable concentration.

The best results are obtained when the concentration is so chosen that the lower half of the slit, for adjustment to equal intensity, must be narrowed from the division 100 to from 30 to 10 on the micrometer; the value of J' then becomes 0.3 to 0.1. If the solution is so slightly colored that J' amounts to more than 0.3 (about

0.5 or 0.6), then the accuracy may be increased by adjusting the micrometers on 50 instead of 100, corresponding to a half turn of the screw. The value thus obtained for J' must be multiplied by 2.

The widths of the slits should not exceed 100 divisions; in case the solution is too concentrated, it should be diluted, or better, a stronger light, the Auer or electric light, should be employed.

Inasmuch as the absorption ratio $A = \frac{c}{e}$ undergoes a slight change in many cases, and apparently depends upon the degree of ionization * for electrolytes (electrolytic dissociation), the value of A must be determined for different concentrations when an accurate study of the absorption ratio is undertaken.

Uses of the Hüfner-Albrecht Rhomb in the Method of Vierordt.—This recently † proposed improvement of the Vierordt spectrophotometer may be appropriately considered here.

The double slit D (Fig. 81), provided with the regular micrometer screws m_1 and m_2, is fastened on the collimator S. A is the liquid vessel with the Schultz glass prism g, which rests on a micrometer stand. The glass rhomb R is placed between the liquid vessel and the double slit. The object of interposing this body is to separate the two spectra by a sharp, fine line, and thus avoid the disturbing influence of the rather heavy dividing line which occurred in the preceding method (p. 196).

The rhomb must be adjusted and fastened by means of the screws s_1 and s_2, so that its horizontal edge next to the slit is of the same height and in immediate contact with the dividing line between the two slits, and so that the horizontal section of the rhomb lies in the prolongation of the optic axis of the collimator.

The upper rays of the light $t\,t'$, which pass through the layer of liquid 11 mm. in thickness, fall upon the lower half, and the lower rays $t_1\,t_1'$, which pass through the Schultz glass prism, fall upon the upper half of the slit, the rays t and t_1 coming in contact at the horizontal edge of the rhomb next to the slit. The rays t' and t_1', which illuminate the lowest and uppermost portions of the slit,

* J. Traube, Ber. d. d. chem. Ges. 25, p. 2989, 1892.

† Krüss, Zeit. anorg. Chem. 1, p. 122, 1892.

leave, on their passage through the liquid vessel, a free space several millimeters broad, into which the upper surface of the prism *g* may be shoved without producing the troublesome conditions previously mentioned. See Hufner, Zeit. phys. Chem. 3, p. 563, 1889, in regard to the use of the rhomb.

Inasmuch as the upper half of the slit is illuminated by the lower light in this method, the lower measuring screw m_2 should be placed

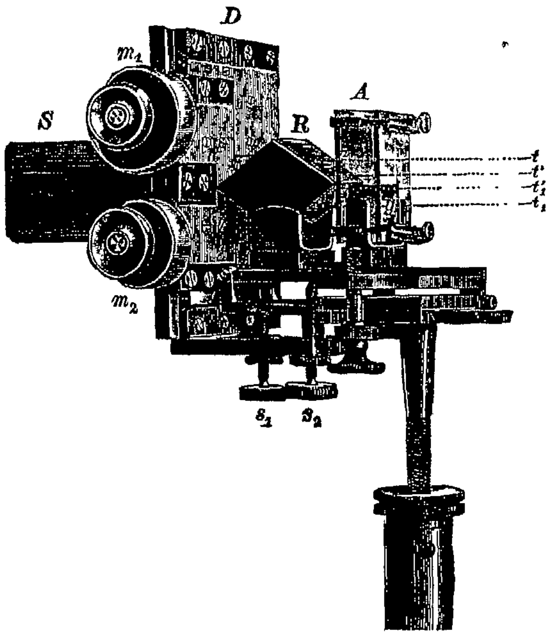

FIG. 81.

on 100, and the upper half of the slit (provided with the larger screw-head m_1) is adjusted so that the intensities of the illuminations are equal (pp. 196, 198, and 199).

Before the experiment is begun, the source of light must be placed (p. 196) so that the upper and lower spectra are of equal intensities when the slits are of equal widths. The rhomb *R* should be protected from foreign light by covering it with a cap.

The following results, obtained by G. Krüss for the spectrum of potassium permanganate, may be noted:

Spectrum region	1 c.c. of solution contains 0.00025 gm.		0.000125 gm.		0.0000625 gm.		Absorption ratio
	J'	e	J'	e	J'	e	A
λ 494.7 — λ 486.5	0.043	1.36654	0.230	0.63828	0.477	0.32149	0.0001909
λ 486.5 — λ 480.9	0.076	1.17393	0.287	0.54212	0.539	0.26842	0.0002251
λ 480.9 — λ 474.8	0.154	0.81248	0.440	0.35655	——	——	0.0003277.

The mean of all the extinction-coefficients in one spectrum region for the different concentrations is used in the calculation of the absorption ratio.

The polarization-spectrophotometer of Glan, and especially of Hüfner, is used as frequently, perhaps, as the spectrophotometric method of Vierordt. Glan, Wied. Ann. 1, p. 351, 1877; Hüfner, Jour. prakt. Chem. (2) 16, p. 290, 1877; and Zeit. phys. Chem. 3, p. 562, 1889. On the comparison of the two methods, see G. and H. Krüss, Kolorimetrie und quantitative Spektralanalyse, and Krüss, Zeit. anorg. Chem. 1, p. 104, 1892. The disadvantage of the polarization-spectrophotometer, owing to the greater loss of light, may be overcome somewhat by the use of the Auer gas-light.

Application of Absorption Spectra.—The qualitative and quantitative investigations of absorption spectra may be applied in the following directions:

1. It is frequently possible to accurately determine the concentration of colored solutions from the extinction-coefficient e and the absorption ratio

$$A = \frac{c}{e}.$$

When A is known (if necessary, for several concentrations), the concentration may be calculated from the extinction-coefficient e by means of the formula $c = A\,e$. See G. and H. Krüss, Kolorimetrie und Spektralanalyse, 1892.

2. Absorption-spectra are of great analytical value for identifying elementary and complex substances.

On elementary spectra, see, among others, Krüss and Nilson, Ber. d. d. chem. Ges. 20, p. 2134, 1887; on the significance of the maximum darkness for the identification of color substances, see page 187.

3. Absorption spectra are closely related to the constitution of the compounds. See Kock, Wied. Ann. 32, p. 167, 1887; G. Krüss, Zeit. phys. Chem. 2, p. 312, 1888; *ibid.* earlier literature; C. Liebermann, Ber. d. d. chem. Ges. 21, p. 2527, 1888; Hartley, Jour. Chem. Soc., p. 641, 1888; Althausse and Krüss, Ber. d. d. chem. Ges. 22, p. 2065, 1889; Schütze, Zeit. phys. Chem. 9, p. 109, 1892; Grebe, *ibid.* 10, p. 673, 1892; Weigle, *ibid.* 11, p. 22, 1893.

4. Absorption phenomena are of special interest in the theory of solutions. Walther, Wied. Ann. 36, p. 518, 1889; Rigollot, Compt. rend. 112, p. 38, 1891; Knoblauch, Wied. Ann. 43, p. 738, 1891; Ostwald, Zeit. phys. Chem. 9, p. 579, 1892; Lellmann, Lieb. Ann. 270, p. 204, 1892.

XIX. ROTATION OF THE PLANE OF POLARIZATION.

General.—The particles of ether in a ray of ordinary light vibrate in different directions perpendicular to the line of propagation, while in plane polarized light the particles vibrate in a single plane. This plane is called the plane of polarization.*

Light may be polarized in various ways: very simply by allowing a ray of ordinary light to pass through a Nicol prism. This consists of a definite combination of two sections of Iceland spar (Landolt, Optisches Drehungsvermögen, p. 3, 1879), so that the entering ray of light is divided into two polarized rays, and so that only the one (extraordinary) ray passes through the prism, while the other (ordinary) ray is removed by total reflection.

If two such Nicol prisms are placed in similar positions in a tube, the polarized ray of light which leaves the first prism will

* According to Fresnel, the particles of ether vibrate perpendicular to the plane of polarization; the above assumption of Neumann, owing to its greater simplicity, will be taken here.

also pass unobstructed through the second prism; if the second prism is rotated through an angle of 180°, the ray will still pass through, for the planes of polarization of the two prisms are parallel for this position. If, however, the second prism is rotated through 90 or 270°, the planes of polarization of the two prisms will be perpendicular to each other, and the light which passes through the first prism will be completely extinguished by the second. If the eye is placed behind the second prism, and one of the prisms is rotated through 360°, four positions 90° apart will be seen to be positions of maximum light and maximum darkness, while the intermediate positions will exhibit varying degrees of illumination.

The first prism is called the polarizer; the second, situated next to the eye, the analyzer.

If the polarizer and analyzer are illuminated with homogeneous light and adjusted to the positions of maximum darkness, and a transparent substance—a liquid in a tube—is introduced between them, the dark field of view in many cases becomes illuminated, and one of the prisms must be rotated through a definite angle to again restore the maximum darkness (principle of the simple polarimeter).

One speaks of the rotation of the plane of polarization of a substance and of the angle of rotation, distinguishes optically active and inactive substances, and calls the substance dextro- or levorotatory, according to the sense of the rotation—*i. e.*, according as the analyzer must be rotated to the right or left to restore the maximum darkness (p 208).

Specific Rotatory Power.—The rotatory power of liquids and dissolved substances only will be considered here.

The amount of rotation of the plane of polarization depends:

1. On the nature of the substance.

2. On the number of optically active molecules, which influence the ray of light; for homogeneous liquids, therefore, on the length of the column and density of the liquid through which the light passes; for solutions, on the length of the column and the concentration.

3. On the wave-length of the light used in the observations.

4. On the temperature at which the observation is made.

5. On the nature of the solvent, in the case of solutions

Let a represent the angle of rotation—*i. e.*, the angle through which the analyzer must be rotated to the left or right to restore the original condition, after interposing a tube filled with an optically active liquid; let d be the density of the liquid, and l the length of the column of liquid, then

$$[a] = \frac{a}{l\,d}$$

is called the specific rotatory power, or the specific rotation of a homogeneous liquid.

The specific rotatory power may be defined as that rotation of the plane of polarization produced when the light passes through an optically active substance 1 dm. in length, which contains 1 gm. of substance per c.c. of volume.

The molecular rotatory power represents the rotation produced by one gram-molecule of the substance under the conditions mentioned for the specific rotatory power.

We have then:

$$[m] = \frac{m\,a}{100\,l\,d} = \frac{m\,[a]}{100}.$$

The values are divided by 100 to avoid large numbers.

If c is the number of grams of substance contained in 100 c.c. of a solution, the specific rotatory power for the given concentration is calculated by the formula:

$$[a] = \frac{100\,a}{l\,c};$$

likewise

$$[m] = \frac{m\,a}{l\,c}.$$

If p grams of substance are contained in 100 gm. of solution, and the density of the solution is d, then the specific rotatory power is

$$[a] = \frac{100\,a}{l\,p\,d}$$

and the molecular rotatory power is

$$[m] = \frac{m\,a}{l\,p\,d}.$$

The calculations for solutions are frequently made according to the above formulas; however, the temperature, the concentration, and the solvent should be considered.

In general, the specific rotation of a substance is in no way proportional to the concentration of the solution. The value of $[\alpha]$, therefore, should be calculated for different concentrations, and the relation of the specific rotation to concentration expressed by formulas of the form $[\alpha] = A + Bq$ and $[\alpha] = A + Bq + Cq^2$; where q is the number of grams of the solvent in 100 gm. of solution, and A, B, and C are constants, the values of which can be easily determined from three or more determinations of $[\alpha]$ for different values of q. A is the true specific rotatory power of the pure substance, for in this case $q = 0$.

In order to determine whether the two- or three-constant formula is to be used, $[\alpha]$ should be determined for widely varying concentrations, and the relation of $[\alpha]$ to q represented graphically by placing the corresponding values in a system of coördinates (p. 186). If the curve is a straight line, the formula $[\alpha] = A + Bq$ should be employed; otherwise the formula

$$[\alpha] = A + Bq + Cq^2$$

is used; *e.g.*, for tartaric acid the first formula is used; for sodium light it becomes $[\alpha] = 1.950 + 0.1303\, q$.

If the true specific rotatory power of the dissolved substance is to be determined as accurately as possible, the substance should be dissolved in an inactive solvent which permits of very high concentrations. The observations should be made with several solvents. The more concentrated the solution is, the smaller are the deviations in the values of $[\alpha]$ calculated for the given concentration and for the pure substance. The true specific rotatory power can not be calculated for sparingly soluble substances. It is sufficient in such cases to establish the above interpolation-formulas which show the dependence of the specific rotatory power on the concentration.

Sodium light is usually employed in these observations; the less intense lithium light or the too volatile thallium light are seldom used. When lithium light is used, a red glass is placed between the flame and the apparatus to hold back the yellow rays. The kind of light used is indicated by a sub-index, thus $[\alpha]_D$ (specific rotation for sodium light); $[\alpha]_{Li}$ for lithium light, etc.

If the observations are to be made with light in other portions of

the spectrum, a combination of polariscope and spectroscope is used (Landolt, Drehungsvermögen, p. 119, 1879).

The light used should be as constant as possible and of as great an intensity as possible.

A lamp similar to that represented in figure 82 may be used to produce homogeneous sodium light. *a* is a Bunsen burner, *b* a chimney with an opening in one side, and *d* a movable rod, to which is fastened a platinum wire and a platinum-gauze spoon. Common salt is melted in this spoon and volatilized in the hottest portion of the flame.

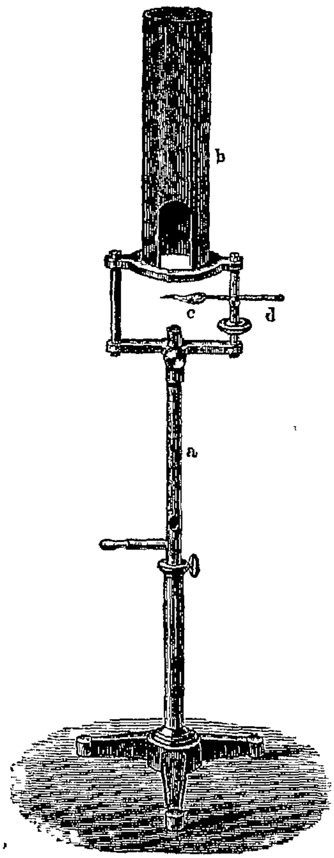

FIG 82.

The following simple contrivance is also to be recommended for producing a strong and lasting sodium light:

A strong platinum wire is covered with platinum gauze. The necessary sodium chloride, or, better, sodium bromide, on account of the greater intensity of light, is fused, finely powdered, and placed in a platinum boat. The platinum gauze is then heated to redness and rolled in the sodium salt. A Münke burner is used as the source of light (p. 186).

Influence of Temperature, Liquid-tube, and Liquid.—An elevation of 1° in temperature for a column of liquid 2 dm. in length diminishes the angle of rotation several tenths of a degree. The observation temperature, therefore, must be noted for all accurate measurements. It is advantageous to make the observations at a constant temperature of about 20°. This can be easily done

if the liquid-tube is surrounded by a metallic mantle (Fig. 83), which is filled with water during the experiment, and which is provided with a thermometer opening at *d*.

If the apparatus is not provided with this contrivance, tubes of the ordinary form (Fig. 84) are used. These are glass tubes *A*, usually 1 to 2 dm. long; they are ground off at the ends exactly perpendicular to their axes, and are closed by means of parallel

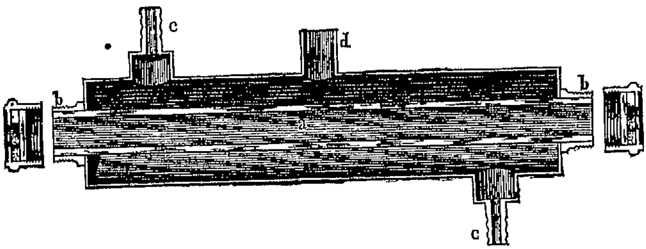

FIG. 83.

glass plates (g_1 g_2), which can be fastened on by means of the screw arrangements m_1 n_1, m_2 n_2.

The glass plate must not be pressed down too strongly, for glass under pressure becomes doubly refracting; this would influence the rotation of the plane of polarization, and hence introduce an error. It is better, therefore, to place a rubber ring on the inner glass

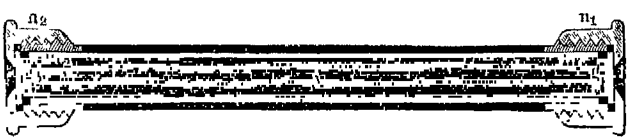

FIG. 84.

surface. In all cases, however, the influence of these plates for new instruments should be tested.

The exact length of the tube should be given by the manufacturer; otherwise see the measuring contrivance of Landolt, Drehungsvermögen, p. 125, 1879.

The tube and glass plates must be carefully cleaned. The presence of air-bubbles must be avoided in filling the tube. The liquid

should be clear. In case of filtration, care must be taken to prevent any change in the concentration of the solution.

Finally, the weights should be given in percentages. For accurate determinations, the weighings should be reduced to the vacuum standard (p. 12). The specific gravity is determined by means of the pyknometer (p. 19). The results should be accurate to the fourth decimal place.

Special attention should be called to the bi-rotation and similar phenomena, according to which the rotatory power of many solutions undergoes a change with time, and frequently becomes constant after the lapse of considerable time (Ostwald, Allgem. Chem., 2. Aufl., Bd. 1, p. 496, 1891, and Sonnenthal, Zeit. phys. Chem 9, p. 656, 1892).

1. THE POLARIMETER OF MITSCHERLICH.

The apparatus (Figs. 85 and 86) consists in its simplest form of a polarizing Nicol *a*, by means of which the light on entering the tube is polarized. The rays of light are made parallel by means of a lens; and, after passing through the empty or filled tube *f*, they enter the second analyzing prism *b*, which is usually fastened to a graduated circular disc (with vernier, p. 215), by means of which the prism can be rotated. Sometimes, as in the figure, the disc is fixed in position; in such cases the vernier is fastened to the prism and may be rotated by means of the handle *c*.

The observations are carried out in a (at least, partially) darkened room; foreign light may be excluded by a black screen placed behind the sodium light.

The empty tube is first placed in the apparatus, the analyzer rotated through 360°, and the two positions, 180° apart, are determined for which the Nicols are crossed (positions of maximum darkness). The field of view then appears somewhat like figure 87; black streaks occur in the middle of the field. The zero of the scale can be adjusted to this position by rotating the polarizer with the help of the screw *e*; this adjustment, however, is usually made by the manufacturer.

After determining the zero point, the tube is filled with liquid, and the angle measured through which the analyzer must be

rotated to the right or left to restore the condition of maximum darkness.

If the angle, calculated from the zero point, is smaller when the analyzer is turned to the right than when turned to the left, a dextrorotatory substance is usually present, while in the opposite case a levo body is present. If, for example, the analyzer must be rotated 40° to the right or 140° to the left to restore the maximum darkness, the substance is dextrorotatory.

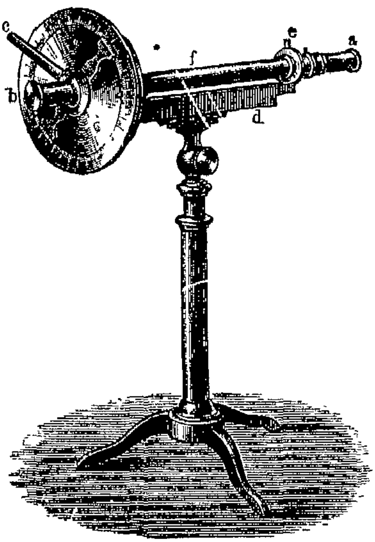

FIG 85.

To determine this with certainty, in doubtful cases, where considerable rotation is produced, a tube of half the length or a solution of half concentration is used. The rotation then will be only half as great as in the first case. In the above example therefore, the analyzer must be rotated 20° or 200° to the right, or adjusted from the left to the numbers 110° or 290°, then :

$$290° = 360° - \frac{140°}{2}.$$

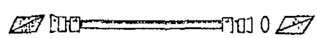

FIG 86.

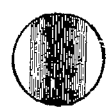

FIG 87

For accurate measurements a large number of observations should be made, and the adjustment made for the two positions of maximum darkness, 180° apart; the results obtained frequently show slight variations. The differences between the separate observations usually amount to several tenths of a degree.

The Mitscherlich apparatus has been modified in recent times

somewhat on the principle of the half-shadow instrument. A small telescope is placed in front of the analyzer and a quartz plate of definite thickness is introduced behind the polarizer. On rotating the analyzer, the two halves of the field of view become evenly and unevenly shaded, as in the case of the Laurent and Lippich apparatus described farther on. This new construction of the Mitscherlich apparatus is more sensitive than the older form.

2. THE POLARISTROBOMETER OF WILD.

This apparatus (Figs. 88 and 89) is capable of sharper adjustment than that of Mitscherlich.

A Savart plate* *s*, formed of two quartz or calcite plates, is placed between the polarizing and analyzing Nicols. A number of dark interference bands (Fig. 90) are produced by this plate, which vanish for definite positions of the prisms. In the measure-

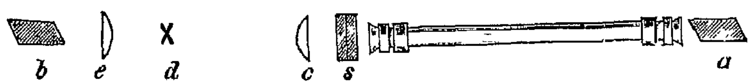

FIG. 88.

ments, the instrument is adjusted to these positions of maximum illumination.

The polarizer, which is illuminated by sodium light, is fastened to the graduated disc *E* provided with a vernier; this disc can be rotated by means of the knob *P* fastened to the toothed rod *Q*. The readings are made by means of the telescope *T*, in which is placed at *V* an inclined mirror, which reflects the light from a small gas-flame onto the vernier. It is to be noticed, inasmuch as the polarizer is rotated, that a rotation of the disc *E* to the left, and therefore of the knob *P* to the right, corresponds to a dextro-rotatory substance.

The zero point is adjusted by determining, during the rotation of *Q*, the four positions 90° apart, for which the interference bands

* Wüllner, Physik, 3. Aufl., Bd. II, p. 604, 1875.

(Fig. 90) vanish. By means of the screw *M* these positions can be made to correspond with the scale divisions 0°, 90°, 180°, and 270°, provided this adjustment has not already been made.

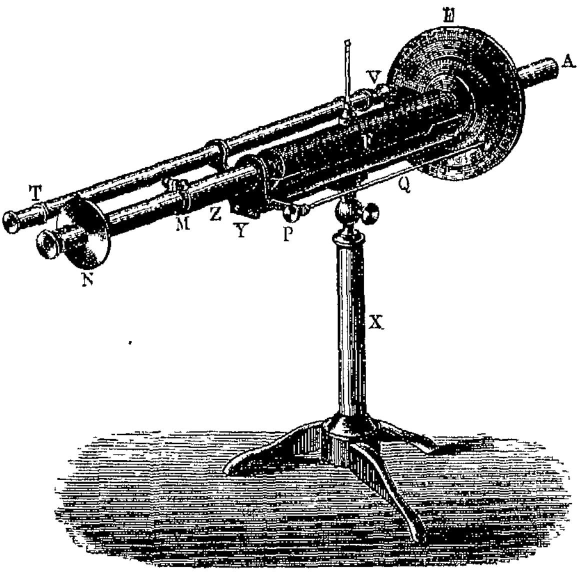

FIG. 89.

The instrument can be adjusted very sharply to the maximum illumination. The apparatus is provided with a small cross-wire telescope (Fig. 88, *c*, *d*, *e*), the eye-piece of which is focused sharply on the cross-wires. In adjusting to maximum illumination the cross-wires should be placed symmetrically with reference to the darkened edges of the field of view.

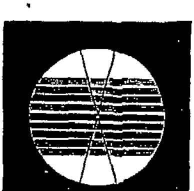

FIG. 90.

The direction in which the substance rotates the plane of polarization is determined as on page 208, greater care being necessary, however, owing to there being four zero points.

Let the zero points be 0°, 90°, 180°, and 270°, and, after introducing the filled tube, suppose the positions of maximum illumination to be 40°, 130°, 220°, and 310°; a rotation of 40° to the right or 50° to the left is to be considered.

A tube of half-length or solution of half concentration is then examined, and if the substance is dextrorotatory, the positions of maximum illumination will be 20°, 110°, 200°, and 290°, or if levo-, 65°, 155°, 245°, and 335°.

In the case of strongly rotating substances the angle of rotation sometimes amounts to more than 90°. By examining tubes of different lengths, however, it is an easy matter to determine whether the angle is α or $90° + \alpha$.

For extremely accurate work the measurements should be made from each of the four zero points; usually, however, it is sufficient to measure from two points 180° apart. After a little practice, the separate observations should not vary more than a few hundredths of a degree.

The measurements are carried out in a somewhat darkened room. The liquids should be clear; any coloration should, if possible, be avoided.

3. THE HALF-SHADOW APPARATUS OF LAURENT.

The sodium light enters this polarimeter (Figs. 91 and 92) through a diaphragm, which is provided with a plate of potassium bichromate crystal, in order to remove the foreign light which accompanies the yellow light.

On leaving the lens *e*, the rays pass parallel into the Nicol *d*, and then enter a second diaphragm *f*, half of which is covered with a quartz or mica plate of definite thickness cut parallel to the axis. From here the rays pass through the liquid-tube *p* into the analyzer *g*, thence through the lenses *i* and *h* (Fig. 92) of the telescope *K*, through which the observations are made.

The characteristic part of the apparatus is the quartz or mica plate, the thickness of which is chosen so that the rays of sodium light which pass through suffer a change of phase of half a wavelength.

If the polarizer is adjusted so that the plane of polarization of the light is parallel to the axis of the quartz, then for each position of the analyzer the two halves of the field of view will be equally illuminated. If, however, the polarizer is placed at an angle α with

this axis, the plane of polarization of the rays of light which pass through the quartz plate will suffer a like displacement, but in the opposite direction (Landolt, Drehungsvermögen, p. 115, 1879).

For this second adjustment the circular field of view appears divided into two halves (Fig. 93), which for most positions of the

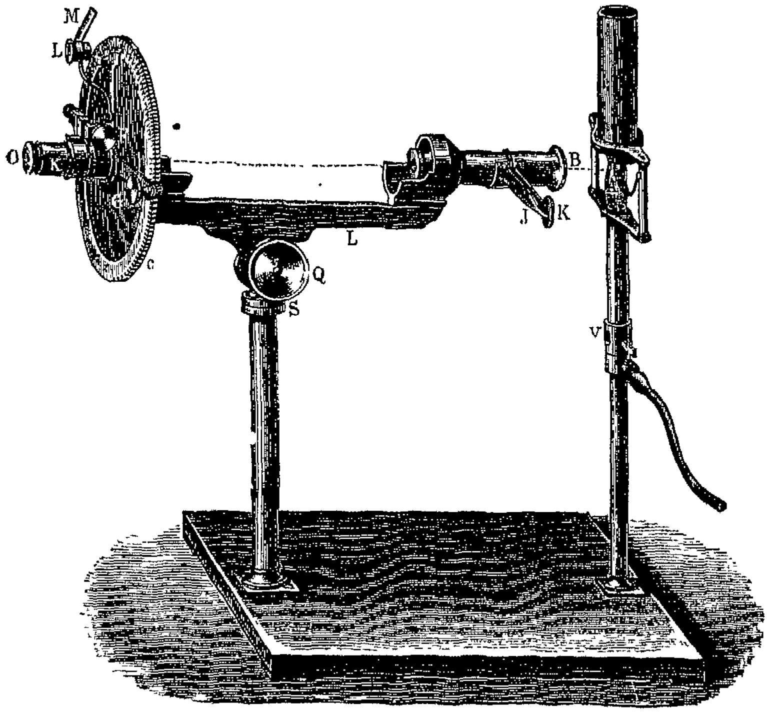

FIG. 91.

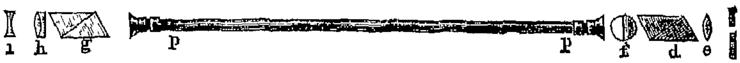

FIG. 92.

Nicol are unequally illuminated (Fig. 93, 1 and 2), but which for two positions 180° apart are uniformly illuminated.

The instrument can be adjusted sharply to this mean, uniform illumination; this is the zero position from which the measurements are made.

The apparatus (Fig. 91) is constructed so that the analyzer, fastened to the telescope and vernier, can be moved by means of an arm on the fixed circle *c*. The vernier is read by means of the microscope *L*.

As already mentioned, the plane of the polarizer must form an angle with the axis of the quartz plate, thereby producing unequal illuminations of the two halves of the field. This is accomplished by means of the contrivance *J K*, by means of which the polarizer can be rotated.

The apparatus is first adjusted to the parallel position, so that for any position of the analyzer the two halves of the field of view are equally illuminated. The polarizer is then rotated through the angle α by means of *J K*. The smaller the angle is, the more sensitive is the instrument; the more brilliant the light and the clearer the liquid, the smaller can α be. The proper adjustment of

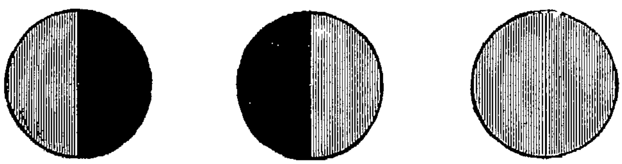

FIG. 93.

the polarizer is that position corresponding to the greatest change of shade in the field of view for a slight movement of the analyzer.

At the beginning of the observation the telescope is focused sharply on the diaphragm, so that the dividing line at the edge of the quartz plate appears sharp.

In determining the zero point the tube should be filled with water, in order that the intensity of the light may be the same as that when the active liquid is observed. In case the field of view is too dark, on account of the liquid being colored or not being clear, the illumination may be increased by a slight rotation of the polarizer; this, however, renders the instrument less sensitive.

If a dextrorotatory substance is observed, the angle on the circular disc will be smaller when turned to the right than when turned to the left; for strongly rotating substances, the method on page 208 is used.

The mean of a large number of results, measured from the two zero points 180° apart, should be taken as the true value.

The apparatus can be used only for sodium light, for the thickness of the crystal plate has already been adjusted for ½ λ.

4. THE HALF-SHADOW APPARATUS OF LIPPICH.

The essential features in the method of operation for the Laurent apparatus apply also to this much-used apparatus.

The main difference in the construction consists in that the quartz plate is replaced in this apparatus by a third Nicol prism, which covers half of the field of view.

On rotating the polarizer by means of an arm, its plane of polarization forms an angle with that of the smaller middle prism. This angle should be as small as possible (p. 213).

This apparatus has the advantage over that of Laurent in that homogeneous light of any wave-length can be used. With the finer construction of this apparatus the angles may be read to 0.001 or 0.002°. On observations with this apparatus, see, among others, Sonnenthal, Zeit. phys. Chem. 9, p. 660, *ibid.* Rimbach, p. 700, 1892.

On the technically important apparatus of Soleil-Ventzke for investigations of sugar, see Landolt, Drehungsvermögen, p. 149, 1879.

Tables of the Rotatory Power, Landolt-Börnstein, Phys. chem. Tab., p. 224, 1883.

The significance of the rotatory power in stereochemistry, see Meyerhoffer, Stereochemie, Leipzig, 1892, and Hantzsch, Grundriss der Stereochemie, Breslau, 1893. The other uses for scientific and technical purposes, especially for determining the concentrations of solutions, see Landolt, Optisches Drehungsvermögen, 1879, and Ber. d. d. chem. Ges. 21, p. 191, 1888. For further recent literature see Hartmann, Ber. d. d. chem. Ges. 21, p. 221, 1888; Pribram, Sitzungsber. Wien. Akad (97) II b, June, 1888, and Ber. d. d. chem. Ges. 22, p. 6, 1889; Long, Sill. Ann. Jour. 36, p 351, 1888, and 38, p. 264, 1889; Sorokin, Jour. russ. Ges. p. 417, 1888; Ref. Zeit. phys. Chem. 4, p. 482, 1889; Kanonnikow, Jour. russ. Ges. pp. 571 and 686, 1888, and p. 369, 1890; Ref. Zeit. phys. Chem. 4, p. 482, 1889, and 6, p. 88, 1890; Sonnenthal, Zeit. phys. Chem. 9, p. 660; Rimbach, *ibid.* 9, p. 700, 1882.

On magnetic rotation, see Perkin, Ber. d. d. chem. Ges. 15, p. 1363, 1882; Jour. Chem. Soc. 45, p. 422, 1884; 52, p. 362, 1887; 53, p. 561, 1888; 55,

p. 680, 1889. Jour. prakt. Chemie N. F. 32, p. 523, 1885; Chem. News 59, p. 247, and 60, p. 253, 1889; 62, p 255, 1890; 64, p. 269, 1891; Jahn, Sitzungsber. Berl Akad. p. 237, 1891, and Wied. Ann. 43, p 280, 1891; Wachsmuth, Wied. Ann. 44, p. 377, 1891, and Schönrock, Zeit. phys. Chem. 11, p 753, 1893.

XX. GENERAL CONTRIVANCES FOR MEASUREMENTS.

1. THE VERNIER (CIRCULAR VERNIER).

The arc *A* (Fig. 94) is fixed in position, while the arc *B*, the vernier, is movable about the central point of the two arcs. *A* is graduated in degrees and half degrees, *B* is divided so that 30 of

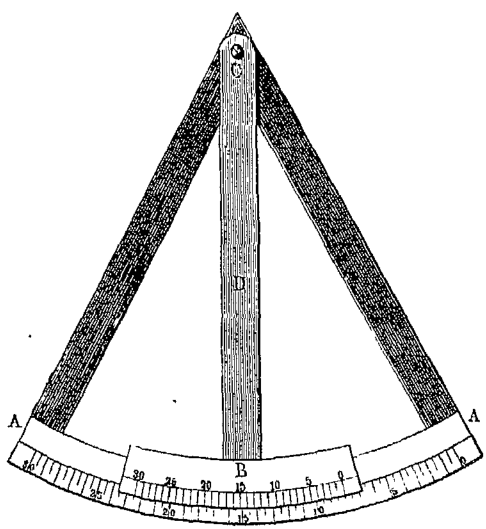

FIG. 94

its divisions correspond to 29 half-degree divisions on the main circle: therefore each division on the vernier is one minute of arc smaller than one division on *A*.

The vernier is adjusted so that its zero point coincides with the zero point of the circle; the first division then is removed 1′, the second 2′, the third 3′, etc., from the corresponding divisions on the circular scale.

If the vernier is rotated through a definite angle, the magnitude of which is to be determined, the number of whole and half degrees through which the index o of the vernier has moved, is read off directly from the main circle.

This reading is sufficient only in case the zero of the vernier coincides with a division on the circle; usually, therefore, a definite number of minutes must be added to the first reading. The number of the division on the vernier which coincides with a division on the main scale, represents the number of minutes to be added.

The vernier is usually read by means of a microscope, which must be placed so that the division to be observed falls in the middle of the field of view. The field of view is illuminated, when necessary, by means of light reflected from a small mirror; a small white paper-screen may also be used for this purpose.

The apparatus with vernier attachment is frequently constructed so that the vernier is fixed and the circle movable.

2. THE CATHETOMETER.

The cathetometer is used to measure the vertical distance between two points.

The column M (Fig. 95) resting on the foot D, which is supported by the screws m_1 m_2 m_3, is movable about its axis.

On this column are two sliding contrivances F and F', with which the telescope B is fastened, and which are connected to the counter-weight Q by means of a cord passing over the pulley T.

The slide F' can be clamped at any desired height by means of the screw K, after which the slide F can be raised or lowered by means of the micrometer screw J. The telescope B provided with the spirit-level L is fastened to F by means of the forks G and G'. The telescope can be leveled by means of the screw o.

In the middle of the column M is an inlaid silver strip, which is graduated in small divisions. By means of a vernier in the opening

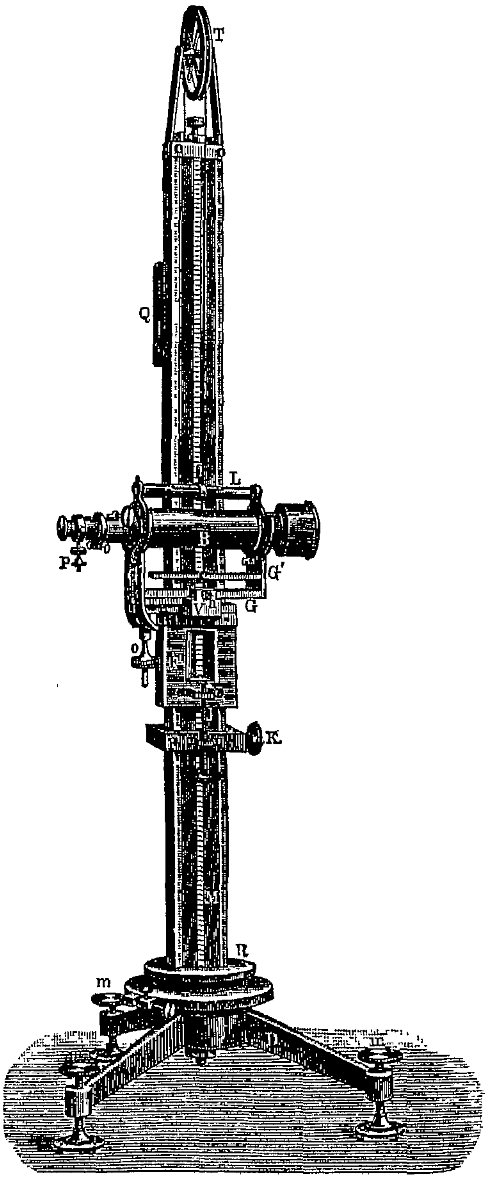

FIG. 95.

at F it is possible to determine the vertical distance between two positions of the telescope with great accuracy.

In carrying out the measurements it is necessary (1) that the axis of the column is exactly vertical; and (2) that the axis of the telescope is exactly horizontal.

To adjust the axis of rotation to a vertical position, the column is turned so that the axis of the telescope is parallel to the line joining m_1 and m_2. After adjusting the spirit-level by means of these screws, the column is turned through an angle of 180°, and the level again adjusted by means of the screw o and the foot-screws m_1 and m_2; the adjustment must be such that the level remains unchanged for these two positions 180° apart. When this is accomplished, the column is rotated so that the axis of the telescope is perpendicular to the line joining m_1 and m_2; the level is then adjusted by means of the screw m_3. The final adjustment must be such that the level remains unchanged during a complete rotation.

To determine whether or not the axis of the telescope is horizontal, the cross-wires of the telescope are adjusted sharply on a definite mark; the telescope is then removed from its position, turned end for end, and replaced in its position. The column is then rotated through 180°, when the cross-wires must again coincide with the mark, provided the axis of the telescope is horizontal. If the cross-wires do not fall exactly on the mark, half of the distance must be corrected by means of the screw o.

3. THE THERMOMETER.

The Beckmann Thermometer.—Besides the ordinary mercury thermometer, the Beckmann thermometer is especially valuable in physico-chemical measurements. This thermometer can not be used for determining definite temperatures, but only for determining definite temperature differences (depression of the freezing point, elevation of the boiling point, thermochemical measurements, etc.).

The thermometer, provided with an arbitrary scale divided into 0.01 or 0.02°, is represented in figure 36, page 82. The characteristic part, the mercury reservoir at the upper end, is shown in figure 96.

By means of this reservoir at the upper end of the thermometer-

tube, the quantity of mercury in the lower bulb of the thermometer can be increased or decreased.

If a definite temperature change is to be measured, the thermometer is heated to approximately the desired temperature; if, then, the mercury thread is too long, the thermometer is heated to 1 or 2° above the temperature, until the thread extends to the mercury in the upper reservoir. By gently tapping the lower end of the thermometer with the hand, the mercury thread is broken off from the excess of mercury in the reservoir. If the quantity of mercury in the lower reservoir should be too small, the adjustment is made in a manner similar to that just described: the thermometer is heated until the thread extends to the mercury in the reservoir, and, after cooling to approximately the desired temperature, gently tapped with the hand, as before.

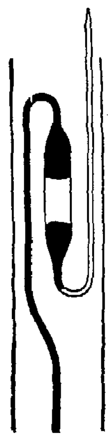

FIG 96.

These and other thermometers, constructed in recent times by F. O. R. Götze, in Leipzig, have been adjusted so that the same thermometer can be used for freezing-point and boiling-point determinations.

It must also be noticed that for such thermometers, owing to the separation of the mercury at higher temperatures, the degree becomes somewhat smaller; the elevation of the boiling point is thereby diminished. Inasmuch as this error may amount to more than 1 per cent., it is necessary for accurate measurements that the thermometer be calibrated, in case the corrections for different temperatures are not known.

Mercury thermometers for measuring temperatures up to 550°, see Recklinghausen, Ber. d. d. chem. Ges. 26, p. 1514, 1893; see, further, The Measurement of High Temperatures, by C. Barus, Leipzig, 1892.

A simple air thermometer: Lothar Meyer, Ber. d. d. chem. Ges. 26, p. 1050, 1893.

Thermometer Testing and Temperature Corrections.—The testing and correcting of thermometers may be divided as follows: (*a*) Determination and correction of the zero point; (*b*) the boiling point; (*c*) correction for the value of the degree;

(*d*) correction for the projecting thread of mercury; (*e*) correction of the caliber error.

Determination of the Zero Point.—The thermometer is kept for a considerable time at a temperature not much above 0°, packed in melting snow or immersed in pulverized ice moistened with distilled water. The water formed must be carefully removed. The determination should also be made by lowering the temperature of the room.

The thermometer is left in the ice for an hour or so, after which the temperature is read. This temperature, equal to that of the ice, is represented by E_0.

If the thermometer is heated to a higher temperature, the capacity of the mercury reservoir increases, owing to the expansion of glass. On subsequent cooling, this change, in many cases, is not completely corrected until weeks or even months have elapsed. This causes a lowering of the position of the mercury, a depression of the zero point, the amount of which depends on the kind of glass, the temperature to which it has been heated, and the length of time heated. After heating for some time at 100°, the depression for ordinary glass amounts to 1°, for Jena normal glass a mean of 0.056° (Böttcher, Zeit. f. Instrumentenkunde, p. 409, 1888).

Owing to this depression of the zero point, it is better that thermometers which are to be used for temperatures approximately equal to zero should be kept in a room of as low a temperature as possible, and should be surrounded by snow for a considerable time before use. If the thermometer is to be used for higher temperatures, then the zero point E_{100} should be determined; *i.e.*, the zero point which a thermometer shows after remaining for some time in ice, when the same thermometer, about half an hour before, had been heated to 100°. This zero point is also used as the basis for graduating thermometers. For use at higher temperatures, the zero point is determined for the corresponding temperature; *e.g.*, E_{200}, E_{250}, etc. In such cases the change of the zero point may be considerable. If E_0 and E_{100} are known, and t is a temperature between 0 and 100°, then we have approximately:

$$E_t = E_{100} + \frac{E_0 - E_{100}}{100}(100 - t).*$$

* Landolt, Zeit. phys. Chem. 4, p. 351, 1889.

For thermometers of Jena normal glass the equation is approximately:

$$E_t = E_{100} + 0.00056\,(100 - t).$$

This zero correction must always be subtracted from the observed temperature t.*

Determination of the Boiling Point.—The apparatus represented in figure 97 may be used for this purpose. The thermometer B is fastened in the top of the double-walled vessel $A\ C$, so that the mercury thread, when adjusted to the boiling point, stands at the top of the stopper, and so that the mercury reservoir is at least 2 cm. above the surface of the boiling liquid. The vapor escapes at r; a small water manometer is placed at r' to measure the excess of pressure p in the vapor chamber. The pressure in the apparatus is slightly greater than the atmospheric pressure, owing to the narrowness of the outlet-tube r. After heating for a suitable length of time, the temperature is read off. The barometric pressure is simultaneously read, reduced to 0° (p. 224), and then added to the slight excess of pressure p, which must first be reduced to mercury units. If b is the corrected barometric pressure in millimeters, then the boiling point t of water (between 715 and 770 mm.) is given to 0.01° by the equation:

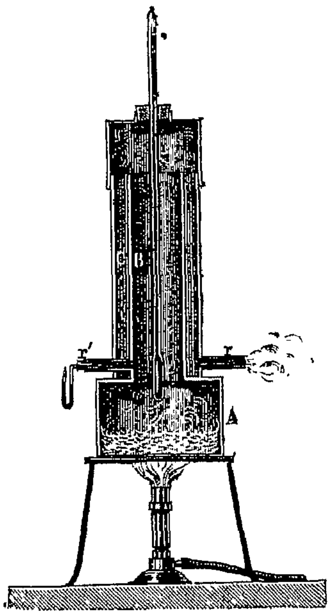

FIG. 97.

$$t = 100° + 0.0375° \,(b - 760).$$

See also Tabellen von Landolt-Börnstein, p. 40, 1883.

Correction for the Degree Value.—If S is the boiling point

* Kohlrausch, Prakt. Phys. VII, p. 82, 1892.

reduced to 760 mm., and E_{100} the freezing point, with a thermometer previously heated to 100°, then the degree value of the thermometer is:

$$G = \frac{100}{S - E_{100}},$$

and the degree-value correction which is to be added to the observed temperature t is:

$$g = (G - 1)\,t.$$

Correction for the Projecting Mercury Thread.—This correction is given by the formula of Landolt,* as follows:

$$f = 0.000131\,(n - 10)\,t,$$

where n is the length of the projecting thread and t is the observed temperature. The correction f is to be added in all temperature measurements.

The corrections for the projecting mercury thread are given in the table (p. 236) calculated by Rimbach for thermometers of Jena glass (graduated to 0.1° for 0 — 100°) and for (0 — 360^{10}°). This correction, however, should be avoided whenever possible.

See Guillaume, Compt. rend. 112, p. 87, 1891, and Mahlke, Zeit. f. Instrumentenkunde 13, p. 58, 1893.

Calibration of the Thermometer.—The errors arising from the unequal diameters of the tube are, especially for high temperatures, of considerable magnitude. For accurate measurements, therefore, the calibration of the thermometer must not be neglected.

For this purpose the mercury thread is broken off from the main quantity of mercury, of such a length a, measured in degrees, that $n = \frac{100}{a}$ is approximately a whole number. For thermometers which are used for high temperatures $a = 50$; in general, $a = 20$ or 10°.

The mercury thread may be broken off by tapping the thermometer after it has been turned upside down. If the thread is too long or too short, the process is repeated, and, inasmuch as the thread usually breaks at the top of the mercury bulb,† its length

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* Landolt, Zeit. phys. Chem. 4, p. 353, 1889.

† To obtain a thread of any desired length, see Kohlrausch, Prakt. Phys. VII, p. 84, 1892.

can be first adjusted by means of ice-water to the desired value and the thermometer then gently tapped.

If a definite interval—*e. g.*, from 0 to 100—is to be calibrated, then the number of scale divisions which correspond to the length of the thread in the different intervals 0 to a, a to $2a$ . . . $(n-1)a$ to 100 must be determined. The thread must be moved in this process from one interval to another, and the readings should be uninfluenced by parallax. The parallax can be avoided by placing the thermometer on a plane mirror and making the reading with the eye in the same straight line with the scale division and its image. The use of a cross-wire microscope provided with a micrometer screw and slide contrivance is still better.

Let E be the zero point and $100 + s$ the boiling point of the thermometer, and suppose the length of the thread in scale divisions for the different intervals to be as follows:

Intervals.	Scale Divisions.
$0 - a$	$a + \delta_1$
$a - 2a$	$a + \delta_2$
: :	: :
$(n-1)a - 100$	$a + \delta_n$, etc ;

then, if we write:

$$\frac{E - s + \delta_1 + \delta_2 + \ldots \delta_n}{n} = \Delta,$$

the correction table* of the thermometer (without regard to the correction of the zero point) is as follows:

Scale Division.	Correction.
a	$\Delta - \delta_1$
$2a$	$2\Delta - (\delta_1 + \delta_2)$
:	
ma	$m\Delta - (\delta_1 + \delta_2 \ldots \delta_m)$.

These corrections are to be added to or subtracted from the corresponding scale divisions according as their values are positive or negative. The results are then represented graphically, and the correction for each degree obtained from the curve.†

General.—When all of these corrections for a temperature

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* See Kohlrausch, Prakt. Phys. VII, p. 86, 1892.

† See also the calibrations of Neumann-Thiesen, Carl's Repert. Exp. Phys. 15, p. 285.

determination have been obtained, it is unnecessary to make a comparison with an air thermometer, and the accuracy of the temperature is increased more than tenfold.

If a good, standard thermometer is at hand, a correction table for any thermometer can be obtained by comparison with the standard. A calibration is then unnecessary.

The two thermometers are fastened together, with their mercury bulbs side by side, and heated to different temperatures in a thermostat. A better method, however, is the simultaneous heating of the two thermometers in the vapors of boiling liquids, whereby the change from one temperature to another can be easily accomplished by means of a good pressure regulator (p. 95).

A microscope, provided with cross-wires, or an eye-piece micrometer, and movable in a vertical direction, should be used for reading the thermometer scale in all accurate determinations. The thermometer should always be shaken or gently tapped before the reading is made. It is also to be observed that the position of the top of the mercury thread, for a definite temperature, deviates slightly, according as the mercury rises or falls to the position in question.

4. THE BAROMETER.

A good barometer (mercury barometer) should be free from air and aqueous vapor.

The top of the mercury is read with the naked eye avoiding parallax, or with a cathetometer.

The most important correction is the reduction of the barometric pressure to 0°. If b is the observed barometric pressure, t the temperature, and 0.000181 the coefficient of cubical expansion of mercury, then the barometric pressure reduced to 0° is $b_0 = b - 0.000181\ b\ t$.

When the expansion of the measuring scale is to be taken into account, the coefficient of expansion of brass can be taken as 0.000019 and that of glass as 0.000008; the barometric pressure is then calculated to 0°:

For a brass scale by the formula $b_0 = b - 0.000162\ b\ t$
" " glass " " " " $b_0 = b - 0.000173\ b\ t$.

(Tables of Landolt-Börnstein, p. 26, 1883).

If the diameter of the barometer-tube is less than about 20 mm., the capillary depression must be taken into account. The corrections for tubes of different diameters are given in Landolt-Börnstein's Tables, p. 21, 1883. These corrections are to be added to the height of the mercury column.

The reduction of the barometric pressure to 45° geographical latitude is, in general, unnecessary for chemical purposes (Kohlrausch, Prakt. Phys. VII, p. 74, 1892).

XXI. TABLES.

TABLE OF ATOMIC WEIGHTS.

ACCORDING TO OSTWALD AND CLARKE,* ON THE BASIS OF O = 16.

	Ostw.	Clk.		Ostw.	Clk.
Aluminium, ...	27.10	27.11	Molybdenum, . .	95.90	95.99
Antimony, ...	120.30	120.43	Neodymium, . . .	140.80	140.80
Argon, ...	...	...	Nickel, ...	59.00	58.69
Arsenic, ...	75.00	75.01	Nitrogen, ...	14.04	14.04
Barium, . .	137.00	137.43	Osmium, ...	192.00	190.99
Bismuth, . . .	208.00	208.11	Oxygen, ...	16.00	16.00
Boron, ...	11.01	10.95	Palladium,	106.00	106.36
Bromine, ...	79.96	79.95	Phosphorus, ...	31.03	31.02
Cadmium, ...	112.10	111.95	Platinum, ...	194.80	194.89
Calcium, ...	40.00	40.07	Potassium, ...	39.14	39.11
Carbon, ...	12.00	12.00	Praseodymium, . . .	143.60	143.60
Cerium, ...	140.20	139.35	Rhodium, ...	103.00	103.01
Cæsium, ...	132.90	132.89	Rubidium, ...	85.40	85.43
Chlorine, ...	35.45	35.45	Ruthenium, ...	103.80	101.68
Chromium, ...	52.20	52.14	Samarium, ...	150.00	150.26
Cobalt, ...	59.00	58.99	Scandium, ...	44.10	44.12
Columbium, ...	94.20	93.73	Selenium, ...	79.10	79.02
Copper, ...	63.30	63.60	Silicon, ...	28.40	28.40
Erbium, ...	166.00	166.32	Silver, ...	107.938	107.92
Fluorine, ...	19.00	19.06	Sodium, ...	23.06	23.05
Gadolinium, . . .	...	156.76	Strontium, ...	87.50	87.61
Gallium, ...	69.90	69.91	Sulphur, ...	32.06	32.07
Germanium, ...	72.30	72.48	Tantalum, ...	183.00	182.84
Glucinum (Beryllium),	9.10	9.08	Tellurium, ...	125.00	127.49
Gold, ...	197.20	197.23	Terbium, ...	...	160.00
Helium, ...	...	...	Thallium, ...	204.10	204.15
Hydrogen, ...	1.007	1.008	Thorium, ...	232.40	232.63
Indium, ...	113.70	113.85	Thulium, ...	171.00	170.10
Iodine, ...	126.86	126.85	Tin, ...	118.10	119.05
Iridium, ...	193.20	193.12	Titanium, ...	48.10	48.15
Iron, ...	56.00	56.02	Tungsten, ...	184.00	184.83
Lanthanum, ...	138.50	138.64	Uranium, ...	239.40	239.59
Lead, ...	206.91	206.92	Vanadium, . . .	51.20	51.38
Lithium, ...	7.03	7.03	Ytterbium, ...	173.20	173.19
Magnesium, ...	24.38	24.28	Yttrium, ...	89.10	89.02
Manganese, ...	55.00	54.99	Zinc, ...	65.50	65.41
Mercury, ...	200.40	200.00	Zirconium, ...	90.70	90.40

* [Clarke's latest report, Jour. Amer. Chem. Soc. 20, p. 171, 1898.—Tr.]

TABLE OF OBACH, ABRIDGED ACCORDING TO OSTWALD.

(ELECTRIC CONDUCTIVITY.)

$\frac{a}{1000-a}$ for $a = 1$ to $a = 999$.

	0	1	2	3	4	5	6	7	8	9
00	1.0000	010	020	030	040	050	060	071	081	091
01	101	111	122	132	142	152	163	173	183	194
02	204	215	225	235	246	256	267	278	288	299
03	309	320	331	341	352	363	373	384	395	406
04	417	428	438	449	460	471	482	493	504	515
05	526	537	549	560	571	582	593	605	616	627
06	638	650	661	672	684	695	707	718	730	741
07	753	764	776	788	799	811	823	834	846	858
08	870	881	893	905	917	929	941	953	965	977
09	989	*001	*013	*025	*038	*050	*062	*074	*087	*099
10	0.1111	124	136	148	161	173	186	198	211	223
11	236	249	261	274	287	299	312	325	338	351
12	364	377	390	403	416	429	442	455	468	481
13	494	508	521	534	547	561	574	588	601	614
14	628	641	655	669	682	696	710	723	737	751
15	765	779	793	806	820	834	848	862	877	891
16	905	919	933	947	962	976	990	*005	*019	*034
17	0.2048	063	077	092	107	121	136	151	166	180
18	195	210	225	240	255	270	285	300	315	331
19	346	361	376	392	407	422	438	453	469	484
20	500	516	531	547	563	579	595	610	626	642
21	658	674	690	707	723	739	755	771	788	804
22	821	837	854	870	887	903	920	937	953	970
23	987	*004	*021	*038	*055	*072	*089	*106	*123	*141
24	0.3158	175	193	210	228	245	263	280	298	316
25	333	351	369	387	405	423	441	459	477	495
26	514	532	550	569	587	605	624	643	661	680
27	699	717	736	755	774	793	812	831	850	870
28	889	908	928	947	967	986	*006	*025	045	*065
29	0 4085	104	124	144	164	184	205	225	245	265
30	286	306	327	347	368	389	409	430	451	472
31	493	514	535	556	577	599	620	641	663	684
32	706	728	749	771	793	815	837	859	881	903
33	925	948	970	993	*015	*038	*060	*083	*106	*129
34	0.5152	175	198	221	244	267	291	314	337	361
35	385	408	432	456	480	504	528	552	576	601
36	625	650	674	699	723	748	773	798	823	848
37	873	898	924	949	974	*000	*026	*051	*077	*103
38	0.6129	155	181	208	234	260	287	313	340	367
39	393	420	447	475	502	529	556	584	611	639
40	667	695	722	750	779	807	835	863	892	921
41	949	978	007	*036	*065	*094	*123	*153	*182	*212
42	0.7241	271	301	331	361	391	422	452	483	513
43	544	575	606	637	668	699	731	762	794	825
44	857	889	921	953	986	*018	*051	*083	*116	*149
45	0.8182	215	248	282	315	349	382	416	450	484
46	519	553	587	622	657	692	727	762	797	832